



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

MAY 17 2012

Samuel B. Boxerman
Sidley Austin LLP
1501 K Street, N.W.
Washington, D.C. 20005

Re: AES Puerto Rico, L.P.

Dear Mr. Boxerman:

This is in response to your letter of March 30, 2012, regarding the AES Puerto Rico, L.P., Guayama coal-fired power plant (the "facility"), in which you inquired about the analysis of a composite sample of coal ash aggregate ("Agremax") collected at the facility during a March 13, 2012, sampling inspection by the U.S. Environmental Protection Agency (EPA), and requested copies of the results of such analysis.

Please be advised that the composite Agremax sample is currently undergoing analysis for leaching, by Liquid-Solid Partitioning as a Function of Eluate pH, EPA Preliminary Method 1313; mercury, by Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry, EPA Method 7473; metals, by Inductively Coupled Plasma-Atomic Emission Spectrometry, EPA Method 6010C; and anions, by Determination of Inorganic Anions by Ion Chromatography, EPA Method 9056A, at the EPA Inorganic Research Laboratory in Research Triangle Park, North Carolina, and the Vanderbilt University Department of Civil and Environmental Engineering Laboratory in Nashville, Tennessee. A copy of the resulting validated analytical data will be transmitted to you upon our receipt. Also, as requested, copies of the relevant Quality Assurance Project Plans are enclosed. Please note that while no further analysis is planned at this time, we may consider additional analysis of the archived sample at some later date.

Your letter referenced the prior characterization of Agremax by AES Puerto Rico, L.P., using the Toxicity Characteristic Leaching Procedure (TCLP) and the EPA Synthetic Precipitation Leaching Procedure (SPLP), stated that the Leaching Environmental Assessment Framework ("LEAF") methods were "experimental" and had not been validated or published in EPA's Test Methods for Evaluating Solid Waste, Document SW-846, and asked why EPA has chosen to use LEAF rather than TCLP to analyze Agremax. As you may know, EPA developed the LEAF methods in response to concerns raised by the National Academy of Science, the EPA Science Advisory Board, and others over the use of single point pH tests such as TCLP and SPLP for evaluating the leaching potential of coal combustion residuals. The LEAF methods, and the rationale behind their development and proposed uses, are well documented. For more information, you may wish to refer to Evaluating the Fate of Metals in Air Pollution Control Residues from Coal-Fired Power Plants, Environmental Science and Technology, 2010, 44, 7351 - 7356; EPA Science Advisory Board letter to EPA Administrator Carol Browner, February 26,

1999, EPA-SAB-EEC-COM-99-002; Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods, November 2010, EPA/600/R-10/170; Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data, December 2009, EPA-600/R-09/151; and EPA Proposed Rule, Disposal of Coal Combustion Residuals From Electric Utilities, Federal Register, Volume 75, No. 118, June 21, 2010, 35128 – 35264. Additionally, please be advised that the LEAF methods passed inter-laboratory validation testing in December 2011, and, pending the anticipated 2012 publication of a Notice of Data Availability in the Federal Register and subsequent evaluation and potential incorporation of any public comment, will be submitted for posting as new methods on the website for EPA's Test Methods for Evaluating Solid Waste, Document SW-846.

You also raised concerns that the LEAF methods “may not be representative of actual conditions where Agremax is used,” stated that the range of pH referenced in a description of the LEAF methods published by Vanderbilt University (with whom EPA collaborated in the development of the LEAF methods) “do not equate to the pH in the actual uses of Agremax or in the local environment, which...can vary across the island,” and asked that EPA explain “why this testing would adequately evaluate the leaching of Agremax in its actual management scenarios.” Please be advised that the pH range in Method 1313 was, in fact, designed to represent the range of possible environmental leaching conditions. For more information, you may wish to refer to Section 4.1.3, Target pH Values, in the above-referenced Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods, November 2010, EPA/600/R-10/170.

Finally, you asked whether EPA has concerns about sites it referenced in previous correspondence with the Puerto Rico Environmental Quality Board, where it believes Agremax has, or may have been used, and requested that EPA identify those sites and provide copies of any testing results obtained at such locations. Please be advised that while EPA does, in fact, have concerns relating to the potential for leaching of heavy metals from the land deposition of Agremax in Puerto Rico, our investigation is currently focused on the leaching behavior of Agremax as produced (i.e., before deposition or use). Accordingly, EPA has not collected any samples of Agremax other than that collected at the facility on March 13, 2012. As requested, I am enclosing a list of the sites referenced in previous EPA correspondence, as well as the locations of several additional sites visited by EPA in March 2012.

We trust that the information provided herein satisfactorily answers your questions. Further, as you may know, EPA was approached during its March 13, 2012, sampling inspection at the facility by Mr. Jon Reimann, AES NA Central, L.L.C., regarding the proposed construction of a federally compliant landfill for future deposition of Agremax. EPA is interested in this proposal and would appreciate receiving a confirmation of these plans, as well more information and specific details on this proposed new facility.

Please be advised that Mr. Gary Nurkin, of EPA's Office of Regional Counsel, is handling this matter for EPA, and may be reached at (212) 637-3195. Additionally, all future correspondence should be directed to Mr. Nurkin at the following address: U.S. EPA, Region 2, Office of Regional Counsel, 290 Broadway, 16th Floor, New York, NY 10007-1866.

Sincerely,



George C. Meyer, P.E., Chief
RCRA Compliance Branch

Enclosure

cc: Manuel Mata, Plant Manager
AES Puerto Rico L.P.
P.O. Box 1890
Guayama, Puerto Rico 00785

Enclosure

**EPA Coal Ash Aggregate Site Visit Locations
Guayama, Salinas, and Arroyo, Puerto Rico**

June 21, 2011

Parque Gabriella II

Porto Bello Plaza

Marbella

Valles de Salinas

Evelymar Development

Dueño Santo Palo Oil

AES Well Field

Los Recreos Plaza

Eta Sigma Alpha, Inc.

Rt. 3, Km. 128.4

March 15, 2012

Rt. 713, Km. 3.3, Cimarona Ward

Cimarona River

Rt. 7707, Km. 3.1, Pozo Hondo Ward

Rt. 3, Km. 142 and Bridge over Guamaní River

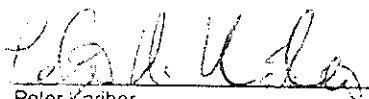


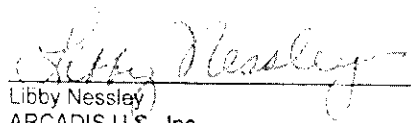
**QAPP for the EPA Interlaboratory
Validation Study of Proposed
SW846 Leaching Methods**

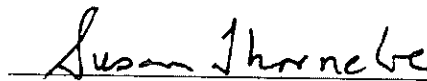
Quality Assurance Project Plan
Category III / Technology Development
Draft

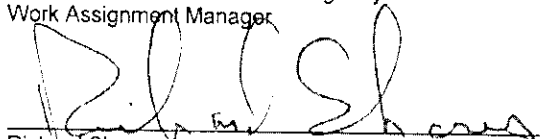
Contract No. EP-C-09-027
Work Assignment No. 2-7

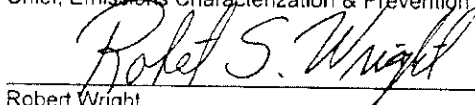
November 2011


Peter Kariher
ARCADIS U.S., Inc.
Work Assignment Leader
10/25/2011
Date


Libby Nessley
ARCADIS U.S., Inc.
Quality Assurance Officer
10/25/2011
Date


Susan Thorneloe
U.S. Environmental Protection Agency
Work Assignment Manager
11/22/11
Date


Richard Shores
U.S. Environmental Protection Agency
Chief, Emissions Characterization & Prevention Branch
11/22/11
Date


Robert Wright
U.S. Environmental Protection Agency
Quality Assurance Representative
11/22/11
Date

**QAPP for the EPA Interlaboratory
Validation Study of Proposed SW846
Leaching Methods**

Quality Assurance Project Plan
Category III / Technology Development
Final

Prepared for
Susan Thorneloe
U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division
Atmospheric Protection Branch
Research Triangle Park, NC 27711

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Our Ref
RN990272.0007

Date:
November 2011

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List of Acronyms and Abbreviations

AA	atomic adsorption
ANOVA	analysis of variance
APPCD	Air Pollution Prevention and Control Division
ARCADIS	ARCADIS, U.S., Inc.
CCR(s)	coal combustion residue(s)
CCV	continuing calibration verification
COPC(s)	constituent(s) of potential concern
CVAA	cold vapor atomic adsorption
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon

DQI	data quality indicator
EC	elemental carbon
EPA	U.S. Environmental Protection Agency
FGD	flue-gas desulfurization
FWHM	full width at half maximum
g	gram
HPGe	high purity germanium
IC	inorganic carbon
ICP	inductively couple plasma
ICV	initial calibration verification
LOI	loss on ignition
MDA	minimum detectable activity
MDL	method detection limit
mL	milliliter
ML	minimum level of quantification
MLQ	minimum level of quantification
MS	mass-spectrometry
NA	not applicable
NCSU	North Carolina State University
NIST	National Institute of Science and Technology
NPOC	non-purgeable organic carbon
OC	organic carbon
OES	optical emission spectroscopy
ORCR	Office of Resource Conservation and Recovery
ORD	Office of Research and Development
OSR	Office of Solid Waste
QAPP	quality assurance project plan
RL	reporting limit
RPD	relative percent difference
RSD	relative standard deviation
SPLP	synthetic precipitation leaching procedure

SW-846	EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods
TCLP	toxicity characteristic leaching procedure
TD	thermal decomposition
TSA	technical system audit
XRF	X-ray fluorescence spectrometry

Distribution List

Copies of this plan and all revisions will be initially sent to the following individuals. It is the responsibility of the U.S. Environmental Protection Agency (EPA) Work Assignment Manager and of the ARCADIS, U.S., Inc. (ARCADIS) Work Assignment Leader to make copies of the plan available to all field personnel.

Susan Thorneloe, EPA Work Assignment Manager. Office of Research and Development, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC.

Phone: (919) 541-2709

Email: thorneloe.susan@epa.gov

Robert Wright, EPA Quality Assurance Officer. Office of Research and Development, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC.

Phone: (919) 541-4502

Email: wright.bob@epa.gov

Peter Kariher, ARCADIS Work Assignment Leader. Research Triangle Park, NC.

Phone: (919) 541-5740

Email: peter.kariher@arcadis-us.com

Libby Nessley, ARCADIS Quality Assurance Officer. Durham, NC.

Phone: (919) 544-4535 x258

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Dr. David Kosson, Methods Development. Vanderbilt University, Nashville, TN.

Phone: (615) 322-1064

Email: David.Kosson@vanderbilt.edu

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Phone: (615) 322-5135

E-mail: Florence.Sanchez@vanderbilt.edu

Dr. Andrew Garrabrants, Methods Development. Vanderbilt University, Nashville, TN.

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Dr. Hans van der Sloot, Methods Development. Hans van der Sloot Consultancy, The Netherlands.

Phone: +31(0)226-341607

Email: hans@vanderslootconsultancy.nl

Dr. Leonard A Stefanski, Statistical Consultant. North Carolina State University, Raleigh, NC.

Phone: (919) 515-1945

Email: stefanski@stat.ncsu.edu

1. Project Objectives and Organization

1.1 Purpose

The Air Pollution Prevention and Control Division (APPCD) of EPA's Office of Research and Development (ORD) is conducting research to evaluate potential leaching and cross media transfers of mercury and other constituents of potential concern (COPCs) resulting from the management of coal combustion residues (CCRs) resulting from wider use of state-of-the art air pollution control technology. This research was cited as a priority in EPA's Mercury Roadmap (<http://www.epa.gov/mercury/roadmap.htm>) to ensure that one environmental problem is not being traded for another. The objective is to understand the fate of mercury and other COPCs and ensure that emissions being controlled in the flue gas at power plants are not later being released depending upon how the CCRs are managed.

As part of this research effort, individual leaching test methods have been developed for inclusion into SW846. These methods were adapted by Dr. David Kosson, Dr. Florence Sanchez, and Dr. Andrew Garrabrants of Vanderbilt University, and their consultant, Dr. Hans van der Sloot from The Netherlands, from the publication titled *An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials* (Kosson et al., 2002, Environmental Engineering Science, Volume 19, Number 3, 159-203). Four test methods have been developed as preliminary versions of EPA methods¹ and can be found at <http://www.vanderbilt.edu/leaching/downloads.html>. The four leaching test methods include:

1. Pre Method 1313: Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure
2. Pre Method 1314: Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using an Up-flow Percolation Column Procedure
3. Pre Method 1315: Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials using a Semi-dynamic Tank Leaching Procedure
4. Pre Method 1316: Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using a Parallel Batch Extraction Procedure

¹ Preliminary Version denotes that this method has not been endorsed by EPA but is under consideration for inclusion into SW-846.

Multilaboratory validation data is necessary for a method to be considered for inclusion in SW-846 (per *Guidance for Methods Development and Validation for the RCRA Program*). This Quality Assurance Project Plan (QAPP) is being written to cover the EPA Interlaboratory Validation Study of the above four proposed SW-846 leaching methods. A separate interlaboratory study will be performed for each of the four methods separately. Due to similarities in equipment and procedures, the first methods to be tested are Pre Method 1313 and Pre Method 1316.

1.2 Project Objectives

US EPA's Office of Resource Conservation and Recovery (ORCR) formerly the Office of Solid Waste (OSW) requires that an interlaboratory validation be conducted for a method to be considered for inclusion into SW-846. This QAPP will detail the process by which each of the four proposed leaching methods will be validated by at least five, and up to ten, different laboratories to establish reproducibility.

The determination of laboratory reproducibility is the final stage in the method development process, prior to the submission of the method for ORCR review. By reproducibility, the Agency means that multiple operators and multiple laboratories should be able to obtain comparable performance data on split samples using the method. It is necessary to demonstrate that satisfactory method performance is not limited to the individual operator or laboratory that developed the method. The minimum number of laboratories that are needed to participate in a multilaboratory method validation is three, with preferably more. Developers of new methods need to do a limited multilaboratory evaluation and provide the individual laboratory and summary performance data in the method submission.

This QAPP is a replacement of the QAPP approved on June 21, 2010 (QTRAK# 03069-A00244). This QAPP will provide details of the following tasks:

- Preparation and characterization of the CCR by APPCD's on-site laboratory support contractor, ARCADIS, prior to distributing to each laboratory participating in the validation study (Task 1)
- Leaching of CCR and other method validation materials (by the proposed SW846 method) by ARCADIS (to establish the baseline results) and by each participating laboratory. All leachates will be submitted to Vanderbilt University for analysis (Task 2)
- Determination of the reproducibility (variability between laboratories), repeatability (single-operator precision) and accuracy of each method (Task 3)
- Leaching of 5 fly ash, 3 scrubber sludge, the 3 other validation materials (foundry sand, solid waste analog, and contaminated field soil), and a cement kiln dust sample using SW-846 Method 1311 "Toxicity Characteristic Leaching Procedure" (EPA, 1992) and SW-846 Method 1312 "Synthetic

Precipitation Leaching Procedure" (EPA, 1994) with analysis for metals by ICP-OES for comparison with the proposed new leaching methods (Task 4)

- Vanderbilt will perform radionuclide testing on 35 fly ash samples, 6 flue-gas desulfurization (FGD) gypsum and 1 cement kiln dust samples to determine uranium species and concentrations by the measurement of Beta and Gamma decay particles (Task 5)

2. Project Organization

The organizational chart for this project is shown in Figure 2-1. The roles and responsibilities of the project personnel are discussed in the following paragraphs. In addition, contact information is also provided. Appendix A identifies the nine laboratories participating in this interlaboratory validation study.

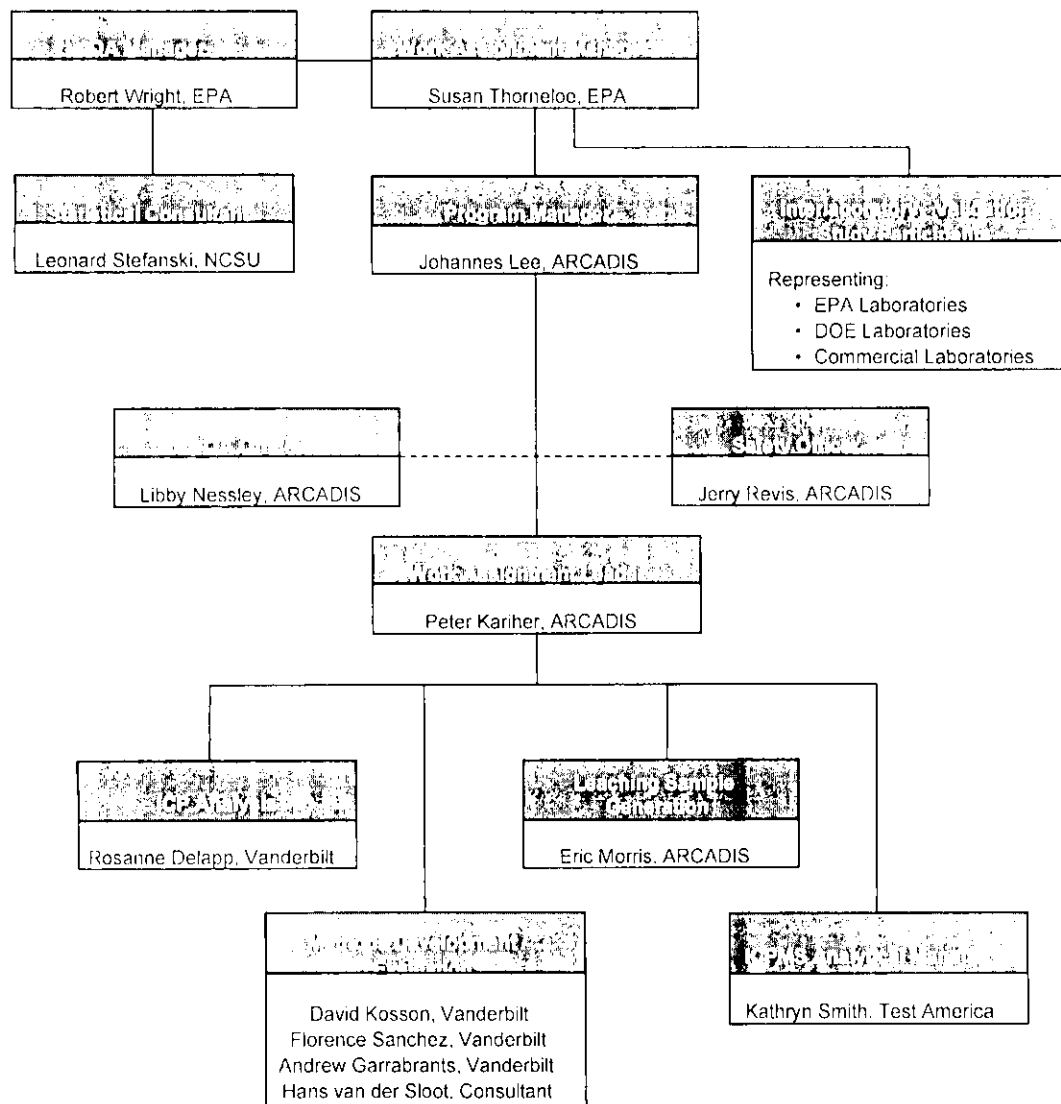


Figure 2-1. Project Organizational Chart

EPA Work Assignment Manager, Susan Thorneloe: The EPA WA Manager is responsible for communicating the scope of work, and is the primary party responsible for review and approval of this QAPP and all other deliverables under this work assignment. The EPA WA Manager is responsible for providing ARCADIS with the various CCR to be used for this interlaboratory validation study. Ms. Thorneloe will also send requests to a number of EPA, DOE and commercial laboratories asking for participation in this interlaboratory study, and will be responsible for making the final selection of which laboratories will be included in the study. She will receive the laboratory data packages, and oversee the evaluation of the results by Vanderbilt, ARCADIS, and the NCSU statistician.

Phone: (919) 541-2709

E-mail: thorneloe.susan@epamail.epa.gov

EPA QA Representative, Robert Wright: The EPA QA Representative will be responsible for reviewing and approving this QAPP. This project has been assigned a QA category III and may be audited by EPA QA. Mr. Wright is responsible for coordinating any EPA audits.

Phone (919) 541-4502

E-mail: wright.bob@epamail.epa.gov

ARCADIS Work Assignment Leader, Peter Kariher: The ARCADIS WA Leader is responsible for preparing project deliverables and managing the work assignment. He will ensure the project meets scheduled milestones and stays within budgetary constraints agreed upon by EPA. The WA Leader is also responsible for communicating any delays in scheduling or changes in cost to the EPA WA Manager as soon as possible. Mr. Kariher, along with Dr. Kosson (Vanderbilt) and Dr. Stefanski (NCSU) will review the laboratory data packages.

Phone (919) 541-5740

E-mail: peter.kariher@arcadis-us.com

ARCADIS Inorganic Laboratory Manager, Peter Kariher: In addition to being the WA Leader, Peter Kariher is also responsible for the operation of EPA's in-house Inorganic Laboratory. Mr. Kariher is responsible for preparation of this QAPP, and will prepare the homogenized CCR(s) to be used in the interlaboratory validation study. He will perform the characterization and leaching of each CCR by Pre-Methods 1313 and 1316 prior to distributing the CCR to the labs for comparative analysis. Mr. Kariher will operate the mercury analyzer and ion chromatograph, and for the leaching studies and mercury and metals analyses, will be supported by one technician: John Foley. Mr. Kariher will perform SW-846 Method 3052 digestion of solid CCR samples and also be responsible for mercury analysis of samples by CVAA. John Foley will perform the leaching tests. Mr. Kariher will submit the remaining Method 3052 digestates to the subcontract analytical laboratory, Test America-Savannah for ICP/MS analysis of the other target metals. He will also be involved with the EPA WAM and the Vanderbilt University methods developers in evaluating the results.

Phone (919) 541-5740

E-mail: peter.kariher@arcadis-us.com

Test America-Savannah Analytical Manager, Kathryn Smith: Ms. Smith will review and validate the ICP/MS results for total content digest samples and report them to Mr. Kariher.

Phone (912) 354-7858

E-mail: kathye.smith@testamericainc.com

ARCADIS Designated QA Officer, Libby Nessley: The ARCADIS QA Manager, Libby Nessley, has been assigned QA responsibilities for this work assignment. Ms. Nessley will be responsible for reviewing this QAPP prior to submission to EPA QA for review. Ms. Nessley will perform an internal data quality audit on at least 10% of the ARCADIS reported data. In addition, she will perform a Technical System Audit (TSA) if requested by the EPA WAM or the ARCADIS WAL. All QA/QC related problems will be reported directly to the ARCADIS WAL, Peter Kariher.

Phone: (919) 544-4535

E-mail: libby.nessley@arcadis-us.com

Vanderbilt University, Methods Development, Professors David Kosson, Florence Sanchez, Andrew Garrabrants, and Rossane Delapp; Consultant, Methods Development, Hans van der Sloot: Dr.

Kosson in cooperation with Dr. Florence Sanchez, Dr. Andrew Garrabrants, and Dr. Hans van der Sloot developed the leachability methods being evaluated during this interlaboratory validation study. All leachates will be sent to Vanderbilt University for analysis by ICP-OES. Ms. Rossane Delapp will assist in the analysis of the leachates for determination of the non-mercury metals concentrations and will develop the LeachXS Lite analytical database for sample data viewing and reporting. Ms. Delapp will also be responsible for the reference lab application of Pre-Methods 1313, 1314, 1315 and 1316. Drs. Kosson, Sanchez, Garrabrants, and van der Sloot will be available to consult with the EPA WAM and ARCADIS Inorganic Laboratory Manager regarding the evaluation of the interlaboratory comparative results for each of the proposed SW846 methods. Dr. Kosson, Dr. Garrabrants, Mr. Kariher (ARCADIS) and Dr. Stefanski (NCSU) will review the laboratory data packages.

Dr. David Kosson

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Ms. Rossane Delapp

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E-mail: rossane.c.delapp@vanderbilt.edu

ARCADIS Project Manager, Johannes Lee: The ARCADIS Project Manager, Johannes Lee, has been assigned financial, contractual and managerial responsibilities for this work assignment. Mr. Lee will be responsible for communications with the EPA project officer, the oversight of financial status, and fulfilling contractual requirements.

Phone: (919) 544-4535

E-mail: johannes.lee@arcadis-us.com

ARCADIS Safety Officer, Jerry Revis: The ARCADIS Safety Officer, Jerry Revis, has been assigned the safety supervisor responsibilities for this work assignment. Mr. Revis will be responsible for reviewing safety plans, performing periodic safety inspections, communicating with the EPA safety office, and oversight of safety operations.

Phone: (919) 544-4535

E-mail: jerry.revis@arcadis-us.com

North Carolina State University (NCSU), Statistical Consultant, Dr. Leonard A Stefanski: Dr. Stefanski will provide statistical consultation on the planning and implementation of interlaboratory study to ensure validity of the collected data. He will also provide advice on the choice and application of statistical methods used to analyze the study data, and on the interpretation of results obtained from the statistical analyses. Dr. Stefanski will report to Mr. Wright, the EPA QA Representative. He will assist Dr. Kosson (Vanderbilt) and Mr. Kariher (ARCADIS) in reviewing the laboratory data packages.

Phone: 919-515-1945

E-mail: stefanski@stat.ncsu.edu

3. Experimental Approach

This interlaboratory comparison will include a comparison of leaching test methods performance by a reference laboratory (either ARCADIS or Vanderbilt) and minimum of six participant laboratories (see Appendix A; nine participant laboratories are currently planned) based on testing of three different materials for each leaching test method to be evaluated. The goal of this study is to determine intra-laboratory and inter-laboratory reproducibility for the four test methods under development. Following is a list of key elements for regulatory methods development as specified in the SW-846 guidance document, and the applicability of each element for this study:

Element 1: Identification of Scope and Application and Regulatory Need

The methods being developed through this study are intended to provide improved leaching characterization of wastes and other materials for use and disposal under a range of field exposure conditions by considering the materials physical characteristics that effect water flow (e.g., granular or monolithic and thus controlling whether water flows through or around the material), and potential field conditions (i.e., pH, water contact mode, liquid-solid ratio). These methods are planned to be applicable for assessments where use of other leaching test methods are not statutorily required.

Element 2: QA/QC Requirements

QA/QC requirements for each method under development are indicated within each method description and are consistent with SW-846 requirements. QA/QC requirements for this study are indicated in this QAPP.

Element 3: Analytical Approach

This study is to evaluate leaching tests (e.g., aqueous extraction tests) that are operationally defined and intended to provide estimation of underlying physical and chemical phenomena controlling constituent release from a solid material to contacting water. Thus, the method of analysis selected for leaching test eluates (i.e., ICP-OES) was a method that was suitably efficient and sensitive for the purposes of this study (see Section 5.2.3). Additional characterization of materials to be tested is being carried out using other analytical techniques (see Section 5).

Element 4: Method/Instrument Sensitivity

Method/instrument sensitivity is based on the chemical analysis technique for leaching test eluates that is selected. This study uses previously standardized methods for chemical analysis.

Element 5: Method Optimization and Ruggedness Testing

An extensive study has been completed that provides an evaluation of related test methods development and optimization based on compilation and evaluation of results from international studies (van der Sloot, et al. 2010). This program is consistent with those findings.

Element 6: Accuracy, Precision and Repeatability (Clean Matrix)

Determination of accuracy is not possible for leaching tests because they are operationally defined and there is no absolute correct value that can be verified using an independent characterization technique. Precision and repeatability for a clean matrix is not possible because of the nature of the materials being evaluated. Instead, intra-laboratory and inter-laboratory repeatability and reproducibility is determined.

Element 7: Effect of Interferences

Method interferences for leaching test methods are either (i) difficulties in physical handling of materials and liquid-solid separation as part of the test method, or (ii) analytical interferences observed during chemical analysis of leaching test eluates. Physical handling and liquid-solid separation difficulties will be noted based on the experience of the participant and reference laboratories. Analytical interferences will be observed based on the analytical QA/QC program (See Section 5) but are not expected based on prior experience testing similar materials.

Element 8: Matrix Suitability

Not applicable.

Element 9: Quantitation and Detection Limits

Determination of quantitation and detection limits is not a goal of this study. Quantitation and detection limits for the chemical analysis techniques to be used in this study are provided in Section 5.

Element 10: Laboratory Reproducibility

This element is the primary focus of this study and addressed as part of this QAPP.

Element 11: Document Submission and Workgroup Evaluation

Data reduction and evaluation is specified in this QAPP. The result will be separate detailed reports documenting results for each test method. An EPA methods workgroup has been formed for these methods following the SW-846 procedures. Mark Baldwin (EPA-OSWR) is the project's liaison with the SW-846 methods workgroup.

The experimental design addresses determining within and between laboratory reproducibility for a set of four leaching test methods. An unbalanced factorial design is being used with appropriate analysis of variance statistical techniques used for data evaluation (see Section 7). Each method will be challenged using three distinctly different materials (coal fly ash, blended Portland cement mortar that includes coal fly ash, metals contaminated soil), selected to reflect a broad range of material properties. Six analytes will be selected for each material to serve as the basis for evaluation. Each analyte will be selected to represent the range of leaching behavior (e.g., concentration as a function of pH and liquid-solid ratio) typically observed for the material being evaluated and be readily detected using a single analytical method (i.e., ICP-OES). Each method is being treated as a separate evaluation from the other methods. Each material evaluated will also be treated statistically as independent evaluations because of the wide range in leaching behavior of individual constituents from material to material (these variations can span several orders of magnitude). Within the statistical design for each method evaluated, the principal factor is testing laboratory (a minimum of 6 independent laboratories and a reference laboratory). The selection of a minimum of 6 independent laboratories is consistent with ASTM recommendations (ASTM, 1988). The reference laboratory and each independent laboratory will carry out the designated test method 6 times and 3 times, respectively, on each material to determine intra-laboratory reproducibility and inter-laboratory reproducibility based on intra-laboratory and inter-laboratory variance. Individual laboratory bias will be evaluated based on deviation from the mean values observed across all laboratories and the statistical significance of the deviation. Each analyte will be treated independently for statistical analysis purposes.

The following discussion is specific to a coal fly ash as an example of the approach that will be used for preparation and evaluation of all materials selected for the study. Coal fly ash from a single facility will be the first material used in this study.

3.1 Task I: Preparing Homogenized CCR

An energy facility, which participated with EPA in an earlier study, has agreed to provide twenty-five, 5-gallon buckets of raw ash for this interlaboratory validation study. The raw ash being supplied this time is from the same facility that was included in an EPA study focused on leaching characterization of a range of CCRs, thus providing extensive useful information on approximate testing results (EPA, 2009). ICP-OES was used to analyze these samples. A list of eight metals have been selected (As, Sb, Ba, B, Ca, Cr, Co,

Mo, Se, and V) as the focus of the intercomparison study, and their method detection limits (MDL) and quantitation or reporting limits (RL) are shown in Table 3-1. From the previous work, graphs have been generated showing the pH dependent concentration of each metal.

This section details how this CCR will be homogenized, split, and tested to ensure that each participating laboratory receives like samples for analysis.

Table 3-1. MDLs and RLs of the Metals to be Evaluated during the Validation Study

Metal	MDL (µg/L)	RL (µg/L)
As	11.0	35.0
Sb	8.00	25.4
Ba	1.00	3.18
B	1.00	3.18
Ca	2.6	8.3
Cr	1.00	3.18
Co	1.00	3.18
Mo	1.2	3.8
Se	15.0	47.7
V	1.5	4.8

A core sample will be taken from 12 of the 25 homogenized buckets and tested to establish homogeneity and to provide characterization data of the CCR. A summary of this testing is shown in Table 3-2. Detailed descriptions of each testing procedure are presented in Section 5. The initial homogeneity testing will be performed using the XRF analysis as the screening technique. Total mercury by thermal decomposition using the Lumex and total digestion methods will be used to further evaluate the CCR leaching reference material. Although further homogenization occurs for each method – as detailed below – this initial core sampling and characterization testing is used to verify that the starting material (which will be used for all validation testing) is indeed homogeneous. Previous results suggest that silicon, a major constituent of this fly ash, will differ by less than 1%. Other constituents can vary by up to 25%. Wider variation between core sample results would indicate that additional homogenization between buckets would be required before proceeding.

Table 3-2. Characterization Testing to Establish Homogeneity of the CCR

Method	Analytes	Number of Replicates
XRF / solids	Total metals content (%)	Single pellet of twelve core samples
Lumex / solids	Total mercury (Hg)	Triplicate analysis of each core sample
Method 3052 / liquids	Total metals	Four cores, selected randomly
Method 3051 / liquids	Total boron (B)	Four cores, selected randomly
Method 1313 / liquids	Leaching behavior by pH	Aliquots of the four, randomly selected cores
EC/OC* / solids	Elemental and organic carbon	Twelve cores, selected randomly

* Elemental carbon/organic carbon needed for accurate XRF calculations

The percent relative standard deviation (RSD) will be calculated with an RSD<10% for major constituents and RSD<20% for trace constituents considered sufficient homogeneity for use in the study.

Each of the proposed SW846 methods will be tested with this ash as the CCR. The detailed procedure for the further homogenization (to ensure that each laboratory is receiving the exact same material for each method being tested) and distribution for testing for each method is detailed below.

Method 1313: Approximately 40 kg (two 5-gallon pails) of material will be combined into a single mixing drum, mixed and then subdivided into approximately 1-kg (1 L) subsamples. Subdivision of the mixed batch into portions will be by coring or a similar method to ensure that potential stratification of the mixed batch does not bias the individual subsamples. The result of the homogenization will be approximately forty 1-L subsamples in 1-L wide mouth HDPE containers with screw top lids. Each participating laboratory will receive two randomly-selected 1-L subsamples for the purpose of carrying out 3 replicate Method 1313 tests on the designated material. Four randomly selected 1-L subsamples will be used to conduct 6 replicate Method 1313 tests by the referee laboratory (ARCADIS). The remaining unused subsamples will be archived. For Phase I testing, the designated material is a coal fly ash.

Method 1314: Approximately 60 kg (three 5-gallon pails) of material will be combined into a single mixing drum. Each batch will be mixed and then subdivided into approximately sixty 1-kg (1-L) subsamples. Subdivision of the mixed batch into subsamples will be by coring or similar method to insure that potential mixed batch stratification does not bias the individual subsamples. This homogenization process will result in approximately sixty 1-L subsamples in 1-L wide mouth HDPE containers with screw top lids. Each participating laboratory will receive four randomly-selected 1-L subsamples for the purpose of carrying out 3 replicate Method 1314 tests on the designated material. Eight randomly selected 1-L subsamples will be used to carry out 6 replicate Method 1314 tests by the referee laboratory (Vanderbilt). The remaining unused subsamples will be archived. For Phase I testing, the designated material is a coal fly ash.

Method 1315: Approximately 100 kg (five 5-gallon pails) of material will be combined to at most two batches to be blended in mixing drum. Each batch will be mixed and then subdivided into approximately one hundred

1-kg (1-L) subsamples. Subdivision of the mixed batch into subsamples will be by coring or similar method to insure that potential mixed batch stratification does not bias the individual subsamples. This procedure will result in approximately one hundred 1-L subsamples in 1-L wide mouth HDPE containers with screw top lids. Eight randomly selected 1-L subsamples will be provided to each participating laboratory for purpose of carrying out 3 replicate Method 1315 tests on the designated material. Sixteen randomly selected 1-L subsamples will be used to carry out 6 replicate Method 1315 tests by the referee laboratory (Vanderbilt). The remaining unused subsamples will be archived. For Phase I testing, the designated material is a coal fly ash.

Method 1316: Approximately 60 kg (three 5-gallon pails) of material will be combined into a single mixing drum. Each batch will be mixed and then subdivided into approximately one hundred 1-kg (1-L) subsamples. Subdivision of the mixed batch into subsamples will be by coring or similar method to insure that potential mixed batch stratification does not bias the individual subsamples. The homogenization process will result in approximately sixty 1-L subsamples in 1-L wide mouth HDPE containers with screw top lids. Four randomly selected 1-L subsamples will be provided to each participating laboratory for purpose of carrying out 3 replicate Method 1316 tests on the designated material. Eight randomly selected 1-L subsamples will be used to carry out 6 replicate Method 1316 tests by the referee laboratory (ARCADIS). The remaining unused subsamples will be archived. For Phase I testing, the designated material is a coal fly ash.

Overall Implications: Thirteen 5-gallon buckets of coal fly ash will be used; 260 1-L wide mouth HDPE jars are needed.

Use of Spiked Samples

Spiking of field generated samples with constituents of concern is generally not recommended because of the difficulty of achieving (i) uniform distribution of the constituent spike, and (ii) speciation of the spiked constituent within reference material that is representative of the speciation of the same constituent originally present. However, spiking of a laboratory-generated reference material (e.g., cement stabilized waste form) for specific constituents of interest is practical because the added spikes will be the primary source of the constituent of interest and uniform distribution can be achieved during the slurry mixing process used to create the sample material. Any spiked samples utilized in this study will be approved by the EPA WAM and fully documented in the project report.

3.2 Task II: Leaching of the CCR by Reference Laboratory and the Intercomparison Laboratories

ARCADIS, having extensive experience in these leaching methodologies as documented in earlier studies, will be responsible for producing the reference leaching data. Six of the cores (as described in Section 3.1 for the characterization testing) will be randomly selected as the replicates to be analyzed by the reference laboratory (ARCADIS or Vanderbilt) by the proposed SW846 method. These results will be compared to the

historical data available for this ash (as described in Section 3.1) to establish the reference results for the method being validated.

Each laboratory will be provided with the following:

1. An introductory letter reiterating the purpose of this study and the laboratory's participation
2. A copy of the SW846 method being validated
3. An amount of homogenized CCR which is adequate to conduct three test replicates
4. Method template spreadsheet
5. As recommended by ORCR, each lab will be asked to have their extractions performed by a single operator on a single instrument in a single batch to minimize variability inherent to the determinative method; all leaching test eluates will be analyzed by ICP-OES for selected constituents by Vanderbilt to minimize variability associated with the metals analysis step since the focus of this study is on the leaching test methods not chemical analysis.

The spreadsheet is very user-friendly and walks the participant through each step of the method and provides a standardized mechanism for data entry into a database for this study as well as comparing results of the materials tested in this study to results obtained from other studies. Appendix B contains a printout of the pages in the Method 1313 spreadsheet showing the instructions and each of the data entry sheets. Appendix C contains examples of the introductory letter, instruction sheet, questionnaires for Methods 1313 and 1316, chain-of-custody form, and a page of sample labels sent to each participating laboratory.

Each laboratory will be asked to perform each of the four proposed methods in triplicate (e.g., 9 pH levels + 3 blanks per test = 36 leachates for Method 1313) within one month. The leachates are to be forwarded to Vanderbilt for analysis. In addition, they are to forward the completed data package to the EPA WAM and Vanderbilt, which will include:

- The completed electronic data report forms (provided as Microsoft® Excel spreadsheets)
- Photocopies or printouts of all raw data, laboratory notebook documentation, calculations, results and comments

- A completed questionnaire indicating any deviations from the prescribed method that were necessary, methodology clarifications needed or suggested, personnel time required to complete the method, and any other suggestions.

The tentative schedule for the interlaboratory validation of the method is shown in Table 3-3.

Table 3-3. Tentative Schedule for Interlaboratory Validation of Proposed SW-846 Methods

Milestone	Tentative Date
Receive ash from previously participating facility	Complete in 2010
Initial characterization and baseline testing	Completed in 2010
Lab's receive material for testing	Completed in 2010 and 2011
Labs send leachates to Vanderbilt for analysis	November 2011
Vanderbilt provides results to EPA	December 2011
Provide final reports for the methods testing	January 2012

3.3 Task III: Determination of the Reproducibility of Each Method

Following receipt of the completed data packages from each participating laboratory and the results of the leachate analyses from Vanderbilt, statistical determination of the reproducibility (variability between laboratories) and repeatability (single-operator precision) of each method will be determined. Leach testing results and feedback will be compiled with like data from other laboratories performing the same method, and will be submitted as part of a supportive data package for EPA ORCR method approval.

3.4 Task IV: Testing of Select Materials for Leaching by SW-846 Methods 1311 (TCLP) and 1312 (SPLP)

Testing of some selected CCRs and the materials from the interlaboratory methods validation study will be performed by ARCADIS using SW-846 Methods 1311 "Toxicity Characteristic Leaching Procedure (TCLP)" and 1312 "Synthetic Precipitation Leaching Procedure (SPLP)" for comparison with the proposed new SW-846 methods. Leachate will be sent to Vanderbilt for analysis by ICP-OES. Results from these experiments will be used to show the comparability of leaching behavior between these tests and the proposed new SW-846 methods. TCLP uses a glacial acetic acid and sodium hydroxide buffer solution with a pH of 4.93 ± 0.05 (Extraction Fluid #1) at a 20 to 1 solid to liquid ratio. SPLP uses a weak sulfuric and nitric acid solution with a pH of 4.2 ± 0.05 (Extraction Fluid #1) at a 20 to 1 liquid to solid ratio to simulate leaching for samples east of the Mississippi river. Samples will be tumbled for 18 hours and filtered to remove the solids. The extract will be preserved with 1% nitric acid and analyzed by Vanderbilt University using ICP-OES. Table 3-4 lists the samples currently selected for TCLP and SPLP testing.

Table 3-4. Sample Testing List for TCLP and SPLP

Sample Name	Sample Type
CaFA	Fly Ash
EaFA	Fly Ash
KFA	Fly Ash
UFA	Fly Ash
ZFA	Fly Ash
YSD	Spray Dryer Ash
MAD	FGD + Fly Ash Mix
DGD	Scrubber Sludge
CKD	Scrubber Sludge
SWA	Solid Waste Analog
CFS	Contaminated Field Soil
JaFS	Brass Foundry Sands
CKD	Cement Kiln Dust

3.5 Task V: Testing of Fly Ashes and Cement Kiln Dust for Radionuclide Testing by Germanium Detector

Vanderbilt will perform radionuclide testing on 35 fly ash samples and 1 cement kiln dust sample to determine uranium species and concentrations by the measurement of Beta and Gamma decay particles using a Germanium (Ge) detector made by ???.

4. Sampling Procedures

The following subsections describe the sampling procedures to be used for each task. Whenever possible, standard methods will be followed. In some cases, draft methods may be evaluated and implemented. Each method to be used will be cited and any deviations from the methods will be documented.

4.1 Sample Custody Procedures

The detailed procedures for preparing and distributing the homogenized CCR were presented in Section 3.1. The following types of samples will be generated during these tests:

1. Solid samples for leaching and radionuclide testing: fly ash, solid waste analog, contaminated field soil, brass foundry sands, scrubber sludge, and cement kiln dust
2. Post-leaching and post-thermal desorption of the CCR (solid samples)
3. Leachate samples (liquid samples) for Hg and other metals analysis

Each sample generated will be analyzed in-house or by outside laboratories. Chain-of-custody (COC) procedures will be required, which will include signing and dating of COCs to indicate receipt of samples, and archived of all COCs with other project documentation. CCRs will be logged as they are received by the ARCADIS WAL, Mr. Peter Kariher. Information regarding where each CCR originated and any other descriptive information available will be recorded in a dedicated laboratory notebook by Mr. Kariher. A core sample will be taken from each 5-gallon bucket of homogenized material and processed for physical and chemical characterization (see Section 3.1). All samples will be properly contained and identified with a unique sample ID and sample label. Chain-of-custody forms will be generated for all samples prior to transfer for analysis.

The sample labeling convention used to identify a particular solution consists of numerical identifiers for the material, lab, test method, and test position along with an alphabetical identifier for the test replicate. The layout for the sample label convention is as follows:

Maa-Lbb-131c-Tdd-e (Test Positions T01 through T09)

Maa-Lbb-131c-Bdd-e (QA/QC Blanks B01-B03)

“aa” is a two-digit number starting at zero that identifies the test material (e.g., the Phase I material is M01),

"bb" is a two-digit number starting at zero that identifies the participating laboratory (assigned randomly by EPA-ORCR),

"c" is a single digit number that completes the test method ID (i.e., 1313, 1314, 1315, 1316, TCLP, or SPLP),

"dd" is a two-digit number starting at zero that identifies the test position or QA/QC blank.

"e" is a single letter representing the test replicate (i.e., A, B or C).

Four sets of completed labels were provided to be used for labeling extraction vessels (for the three replicates and a fourth set for replacements as needed) and two sets of 50-mL analytical samples.

For example, **M01-L02-1313-B02-C** would represent Phase I material being validated by the laboratory randomly identified as "02". The sample is from Method 1313, is blank 02, and replicate C.

Handling of CCR samples for the leaching tests (Task III) is described in detail in each of the proposed SW846 methods. These methods can be found on the Vanderbilt University website at <http://www.vanderbilt.edu/leaching/downloads.html>.

4.2 CCR, and Leaching Reference Material Samples

As mentioned, the objective of this validation study is to obtain information on the reproducibility of the preliminary versions of EPA methods for leaching Al, Sb, Ba, B, Cr, Co, Mg, and Zn from CCRs. The facility descriptions will include information on the history/origin of each method validation sample, facility process description, sample type, sampling location, sampling time and method, coal type, operating condition, and sample storage condition. Section 4.1 describes the sampling custody procedure.

4.2.1 Physical and Chemical Characterization Samples

A core sample will be taken from twelve of the 5-gallon buckets of the homogenized method validation material (as described in Section 3.1) and subjected to physical characterization measurements. These 12 core samples will be mixed together using a riffle splitter prior to XRF pellet preparation and analysis. To ensure a good homogeneity of the final composite sample that will be used for the XRF characterization, the first two composite samples exiting the splitter will be reintroduced at the top of the splitter. This procedure will be repeated at least 6 times. At the end, the two resulting homogeneous composite samples will be combined in the same sample container and stored until XRF testing. Method 3052 samples will also be performed on each of the method validation materials to determine variability for trace elements.

4.2.2 Leaching Study Samples

Method validation materials used for leaching studies will not require size reduction to acquire an adequate sample for testing due to the small particle size inherent in fly ash. The size reduction method is outlined in the leaching test methods (<http://www.vanderbilt.edu/leaching/downloads.html>). If the method validation materials are altered in any way prior to leaching studies, a representative sample will be submitted for physical and chemical characterization.

4.3 Leachate Collection

Each of the proposed SW-846 test methods will be used to conduct a leaching study. The proposed methods can be found on the Vanderbilt University website at <http://www.vanderbilt.edu/leaching/downloads.html>. Table 4-1 shows the extraction schedule and the range of tested pHs as outlined in the first study to be conducted on the *Preliminary Version of EPA Method 1313: Liquid-Solid Partitioning as a Function of Extract pH for Constituents in Solid Materials using a Parallel Batch Extraction Procedure*.

Table 4-1. Final Extract pH Targets for Method 1313

pH Target	Rationale
Will Vary*	Natural pH at LS 10 mL/g-dry (no acid/base addition)
2.0±0.5	Provides estimates of total or available COPC content
4.0±0.5	Lower pH limit of typical management scenario
5.5±0.5	Typical lower range of industrial waste landfills
7.0±0.5	Neutral pH region; high release of oxyanions
8.0±0.5	Endpoint pH of carbonated alkaline materials
9.0±0.5	Minimum of LSP curve for many cationic and amphoteric COPCs
12.0±0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
13.0±0.5	Upper bound (field conditions) for amphoteric COPCs
10.5±0.5	Substitution if natural pH falls within range of a mandatory target

*This is the pH of the material as received with only deionized water added (i.e., no acid or base addition).

Table 4-2 shows an example schedule for the extraction setup to be conducted on the *Preliminary Version of EPA Method 1316: Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio for Constituents in Solid Materials using a Parallel Batch Extraction Procedure*.

Table 4-2. Example Schedule for Method 1316 Extraction Setup

A	B	C	D	E	F	G
Test Position	Target LS	Minimum Dry Mass (g-dry)	Mass of "As-Tested" Sample (g)	Moisture in "As-Tested" Sample (mL)	Volume of Reagent Water (mL)	Recommended Bottle Size (mL)
T01	10.0	20	22.2	2.2	198	250
T02	5.0	40	44.4	4.4	196	250
T03	2.0	100	111	11.1	189	500
T04	1.0	200	222	22.2	178	500
T05	0.5	400	444	44.4	156	1000
B01	QC	—			200	250
Total		—	844		1120	

- NOTE:** 1) This schedule assumes a target liquid volume of 200 mL.
 2) This schedule is based on "as tested" solids content of 0.90 g-dry/g.
 3) Test position marked B01 is a method blank of reagent water.

To demonstrate the versatility and robustness of the proposed new leach test methods, various solid materials other than CCRs were chosen for testing. Table 4-3 shows the proposed test methods and each of the materials to be tested. Table 4-4 gives a brief description of the various solid materials to be tested.

Table 4-3. Materials to be used with the Proposed New Leach Tests

Method	Materials
1313	Fly Ash (EaFA), CFS (Contaminated Field Soil), and SWA (Solid Waste Analog)
1314	CFS (Contaminated Field Soil) and JaFS (Brass Foundry Sands)
1315	SWA (Solid Waste Analog) and CFS (Contaminated Field Soil)
1316	Fly Ash (EaFA), CFS (Contaminated Field Soil), and SWA (Solid Waste Analog)

Table 4-3. Description of Materials for the Proposed New Leach Testing

Material	Description
EaFA	Fly ash from a 2.4 G Watt power plant burning eastern-bituminous coal
CFS	Contaminated field soil collected from an active copper and lead smelting site
SWA	Solid waste analog material containing Type I portland cement, class C coal combustion fly ash, and ground granulated blast furnace slag) and wastewater at a water/binder ratio of 0.41 (m/g). The wastewater used was tap water spiked with powdered metal oxides or metal nitrates of antimony, arsenic, barium, chromium, lead and selenium. This combined material was used to produce both solid monoliths and ground for 2-mm power
1316	Fly Ash (EaFA), CFS (Contaminated Field Soil), and SWA (Solid Waste Analog)
1316	Fly Ash (EaFA), CFS (Contaminated Field Soil), and SWA (Solid Waste Analog)

5. Testing and Measurement Protocols to be Used for Reference Material Characterization and Eluate Characterization

As part of the initial characterization of the raw fly ash CCR, ARCADIS will conduct physical and chemical characterization analyses. In addition, total metals will be analyzed by Test America, and the metals in the leaching extracts will be analyzed by Vanderbilt University. Whenever possible, standard methods will be used to perform required measurements. Standard methods are cited in each applicable section. Where standard methods are not available, operating procedures will be written to describe activities. In situations where method development is ongoing, activities and method changes will be thoroughly documented in dedicated laboratory notebooks.

5.1 Physical Characterization

5.1.1 pH and Conductivity

pH and conductivity will be measured on all aqueous extracts by the laboratory (reference and participant laboratories) carrying out the leaching test method. Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability is dependent upon the presence of ions; on their total concentration, mobility, and variance; and on the temperature of the measurement.

pH of the leachates will be measured by using a combined pH electrode. A 3-point calibration will be done using National Institute of Science and Technology (NIST) traceable pH buffer solutions. The pH meter will be accurate and reproducible to 0.1 pH units with a range of 0 to 14.

Conductivity of the leachates will be measured using a standard conductivity probe. The conductivity probe will be calibrated using appropriate standard conductivity solutions for the conductivity range of concern. Conductivity meters are typically accurate to $\pm 1\%$ and have a precision of $\pm 1\%$. The procedure to measure pH and conductivity will be as follows:

Following a gross separation of the solid and liquid phases by centrifugation or settling, a minimum volume of the supernatant to measure the solution pH and conductivity will be taken and poured in a test tube. The remaining liquid will be separated by pressure filtration and filtrates will be appropriately labeled, preserved, and stored for subsequent chemical analysis.

5.1.2 Moisture Content and Loss on Ignition (LOI)

Moisture content of the raw fly ash CCR will be determined using ASTM D 2216-05 (ASTM 2005) by ARCADIS. This method, however, is not applicable to the materials containing gypsum (calcium sulfate dihydrate or other compounds having significant amounts of hydrated water), since this material slowly

dehydrates at the standard drying temperature (110°C). This slow dehydration results in the formation of another compound (calcium sulfate hemihydrate) which is not normally present in natural material. The ASTM method allows cooling at 60 °C to prevent the conversion and will be used to determine the moisture content of materials containing gypsum.

Loss on ignition (LOI) will be performed on the raw fly ash CCR by placing dried samples in a furnace at 750 °C for 1 hour and measuring the mass lost during the combustion using ASTM D7348-08 (ASTM 2008).

5.2 Chemical Characterization

5.2.1 Dissolved Organic Carbon / Dissolved Inorganic Carbon (DOC/DIC) and Elemental Carbon / Organic Carbon (EC/OC)

Analyses of total dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) will be performed on the leachates as part of the baseline characterization by Vanderbilt University on a Shimadzu model TOC-V CPH/CPN combustion catalytic oxidation NDIR analyzer. Five-point calibration curves, for both inorganic (IC) and non-purgeable organic carbon (NPOC) analyses, are generated for an analytical range between 5 ppm and 100 ppm and are accepted with a correlation coefficient of at least 0.995. Reagent grade potassium hydrogen phthalate is used as the NPOC standard and sodium hydrogen carbonate is used as the IC standard. An analytical blank and check standard at approximately 10 ppm are run every 10 samples. The standard is required to be within 15% of the specified value. A new calibration curve is generated if the check standard measurement does not meet specification. A volume of approximately 16 mL of undiluted sample is loaded for analysis. Inorganic carbon analysis is performed first for the analytical blank and standard and then the samples. Total carbon (non-purgeable organic carbon) analysis follows with addition of 2M hydrochloric acid to a pH of 2 and a sparge gas flow rate of 50 mL/min. Method detection limit (MDL) and minimum level of quantification (MLQ) are shown in Table 5-1.

Table 5-1. MDL and MLQ of Total Organic Carbon Analyzer

	MDL (ppm)	MLQ (ppm)
IC	0.07	0.20
NPOC	0.09	0.20

Elemental carbon (EC) and organic carbon (OC) will be determined on the solids by ARCADIS using a Sunset Laboratory Carbon Aerosol Analysis Lab Instrument in EPA RTP Laboratory E-581A. This method is defined in NIOSH Method 5040 (CDC 2003). This equipment uses a furnace to heat the sample and combust the carbon to carbon dioxide. The carbon dioxide is reduced to methane and a FID is used to quantify the carbon emitted as the sample is heated from ambient to 870 °C over four heating steps.

Samples are prepared by weighing 3 grams of the CCR into a 500 mL Nalgene high-density polyethylene bottle. A 37 mm tarred pre-baked quartz filter is loaded into a 2.5 μm particulate sampler and attached to the bottle. The particulate sampler is connected to a vacuum source and a rotometer to control the flow at 4 liters per minute. The CCR material is aspirated onto the quartz filter for 5 minutes and the filter is reweighed to determine the mass loading. Duplicate filters are prepared for each material. Three analyses are performed on each filter. Blank filters are provided to determine background levels.

5.2.2 Mercury by Thermal Decomposition and Cold Vapor Atomic Adsorption (TD-CVAA) Method 7473

As part of the baseline characterization, mercury analysis of the solid materials will be carried out by ARCADIS using a thermal decomposition cold vapor atomic adsorption (TC/CVAA) according the EPA SW-846 Method 7473 (EPA 1998).

The Lumex RA-915+ Mercury Analyzer is a portable instrument capable of measuring mercury concentrations in air, liquids, and solids. Developed for use by the Russian Navy to detect elemental mercury leaks on submarines (mercury is used as ballast), the analyzer is capable of measuring 1 ng/m³. The instrument contains an internal sample pump, multi-pass optical cell and Zeeman Effect atomic adsorption detector tuned to a wavelength of 253.7 nm for the detection of mercury. The Zeeman effect atomic adsorption (AA) detector modulates the frequency of the source to eliminate matrix effects from air samples and enhance the detector sensitivity for mercury. An optional RP-91C high temperature (>750 °C) furnace can be used to convert any mercury species to elemental mercury for post combustion detection of total mercury in the solids. Since the detector can only measure elemental mercury directly, this technique is based on the thermal decomposition properties of mercury, as only elemental mercury can exist at these high temperatures. Under high temperatures, any oxidized mercury compounds are converted to elemental mercury.

To perform a mercury analysis on a solid sample, the solid of known mass is weighed into a quartz or stainless steel combustion boat. The combustion boat is then inserted into the furnace combustion chamber and as the elemental mercury is evolved from the sample, the detector measures the mass of mercury. The mass of mercury is directly proportional to the area under the peak, similar to the quantitation principle used in gas chromatography. By dividing the mass of mercury by the mass of sample introduced to the instrument, a mercury concentration can be derived. For wet samples, a moisture measurement of the solid must be determined to correct the mercury content to a dry basis.

5.2.3 Other Metals (ICP)

Test America Laboratories in Savannah, GA, will analyze a sample of the raw fly ash for the metal species total content using an Agilent ICP-MS with octopole reaction system (ORS). Vanderbilt University

(Department of Civil and Environmental Engineering) will analyze the metals content of the leachates using a Varian inductively couple plasma optical emission spectroscopy (ICP-OES).

Test America will conduct their total metal analyzes on an ICP-MS using EPA SW-846 Method 6020A (EPA 2007d). Metals and estimated instrument detection limits are listed in the method. The ICP will be profiled and calibrated for the target compounds and specific instrument detection limits will be determined. Mixed calibration standards will be prepared at least 5 levels. Each target compound will also be analyzed separately to determine possible spectral interference or the presence of impurities. Two types of blanks will be run with each batch of samples. A calibration blank is used to establish the analytical curve and the method blank is used to identify possible contamination from varying amounts of the acids used in the sample processing. Additional daily QC checks include an Initial Calibration Verification (ICV) and a Continuing Calibration Verification (CCV). The ICV is prepared by combining target elements from a standard source different than that of the calibration standard and at a concentration within the linear working range of the instrument. The CCV is prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve. A calibration blank and a CCV or ICV are analyzed after every tenth sample and at the end of each batch of samples. The CCV and ICV results must verify that the instrument is within 10% of the initial calibration with an RSD < 5% from replicate integrations. Procedures to incorporate the analysis of a MS/MSD for these CCR samples will be evaluated.

Vanderbilt University (Department of Civil and Environmental Engineering) will also conduct ICP-MS analyses on the reference laboratory leaching test eluates. This will provide a statistical assessment of precision for constituents that are not analyzed for in eluates by the participant laboratories. This will provide precision (intralaboratory, by ICP-MS and ICP-OES) for all elements of concern and reproducibility (interlaboratory, by ICP-OES) for a representative set of constituents. Inferences may be possible concerning the interlaboratory reproducibility for other elements, depending on the relative contributions to variance, between intralaboratory and interlaboratory effects.

A Perkin Elmer model ELAN DRC II will be used in both standard and dynamic reaction chamber (DRC) modes. Standard analysis mode will be used for all analytes except for As and Se, which will be run in DRC mode with 0.5 mL/min of oxygen as the reaction gas. Seven-point standard curves will be used for an analytical range between approximately 0.5 µg/L and 500 µg/L and completed before each analysis. Analytical blanks and analytical check standards at approximately 50 µg/L will be run every 10 to 20 samples and are required to be within 15% of the specified value. Samples for analysis will be diluted gravimetrically to within the targeted analytical range using 1% v/v Optima grade nitric acid (Fisher Scientific). Initially, analyses for 10:1 dilutions will be performed to minimize total dissolved loading to the instrument. Additional dilutions at 100:1 and 1000:1 will be analyzed if the calibration range is exceeded with the 10:1 dilution. 50 µL of a 10 mg/L internal standard consisting of indium (In) (for mass range below 150) and bismuth (Bi) (for mass range over 150) will be added to 10 mL of sample aliquot prior to analysis.

Analytical matrix spikes will be completed for one of each of the replicate eluates from Method 1313. For each analytical matrix spike, a volume between 10 μ L and 100 μ L of a 10 mg/L standard solution will be added to 10 mL of sample aliquot.

ICP-OES Analyses

ICP-OES analyses of aqueous samples from laboratory leaching tests will be carried out at Vanderbilt University (Department of Civil and Environmental Engineering) using a Varian ICP Model 720-ES. Five-point standard curves will be used for an analytical range between approximately 0.1 mg/L and 25 mg/L for trace metals. Seven-point standard curves will be used for an analytical range between approximately 0.1 mg/L and 500 mg/L for minerals. Analytical blanks and analytical check standards at approximately 0.5 mg/L will be run every 10 to 20 samples and are required to be within 15% of the specified value. Initially, analyses will be performed on undiluted samples to minimize total dissolved loading to the instrument. Samples for analysis will be diluted gravimetrically to within the targeted analytical range using 1% v/v Optima grade nitric acid (Fisher Scientific) if the maximum calibration is exceeded. Yttrium at 10 mg/L will be used as the internal standard. Analytical matrix spikes will be completed for three test positions from one of the replicate eluates from Method 1313. For each analytical matrix spike, a volume of 500 μ L of a 10 mg/L standard solution will be added to 5 mL of sample aliquot.

Table 5-2 provides the element analyzed, method detection limit (MDL), and minimum level of quantification (ML). Analyte concentrations measured that are less than the ML and greater than the MDL are reported as estimated value using the instrument response.

Table 5-2. Method Detection Limits (MDLs) and Minimum Level of Quantification (ML) for ICP-OES Analysis on Liquid Samples*

Symbol	Units	MDL	ML
Al	µg/L	1.00	3.18
Sb	µg/L	8.00	25.4
As	µg/L	15.0	47.7
Ba	µg/L	1.00	3.18
Be	µg/L	5.00	15.9
B	µg/L	1.00	3.18
Cd	µg/L	6.00	19.1
Ca	µg/L	3.50	11.1
Cr	µg/L	1.00	3.18
Co	µg/L	1.00	3.18
Cu	µg/L	4.1	13.0
Fe	µg/L	2.90	9.22
Pb	µg/L	7.00	22.3
Li	µg/L	6.00	19.1
Mg	µg/L	1.00	3.18
Mn	µg/L	3.60	11.4
Mo	µg/L	1.00	3.18
Ni	µg/L	2.20	7.00
K	µg/L	1.50	4.77
P	µg/L	6.2	19.7
Se	µg/L	17.0	54.1
Si	µg/L	2.80	8.90
Ag	µg/L	18.00	57.2
Na	µg/L	3.50	11.1
Sr	µg/L	1.00	3.18
S	µg/L	8.30	26.4
Tl	µg/L	5.00	15.9
Sn	µg/L	17.0	54.1
Ti	µg/L	6.40	20.3
V	µg/L	1.30	4.13
Zn	µg/L	2.50	7.95
Zr	µg/L	2.70	8.59

* All elements indicated in Table 5.2 will be analyzed, however, only elements indicated in bold are reported as part of the leaching studies.

5.2.4 X-Ray Fluorescence (XRF)

X-Ray Fluorescence Spectrometry is used in the USEPA RTP, NC laboratories to analyze a sample of the raw fly ash for the determination of total content for the major elements. A Philips model PW 2404 wavelength dispersive instrument, equipped with a PW 2540 VRC sample changer, is used for these analyses. The manufacturer's software suite, "SuperQ", is used to operate the instrument, collect the data, and perform quantification.

The instrument was calibrated using a manufacturer-supplied set of calibration standards at the time of installation of the software plus a new X-ray tube. On a monthly basis, manufacturer-supplied drift correction standards are used to create an updated drift correction factor for each potential analytical line. On a monthly basis, a dedicated suite of QC samples are analyzed before and after the drift correction procedure. This data is used to update and maintain the instrument's QC charts. The SOP for this QC procedure (SOP No. 5003.3; "Procedure for the Philips PW 2404 XRF Monthly Drift Correction, Quality Control Stability Check, QC Chart Update, and Database Backup.") is maintained in a 3-ring binder located at the control module for the spectrometer, along with all other operational SOPs. Any deviations from these QC parameters will be documented to the EPA WAM.

The software suite's "Measure and Analyze" program collects and stores the sample data. This program has two basic modes of operation, "scan" and "channels". The scan mode is used to collect the bulk of the data. It operates in a stepwise scanning mode and uses the manufacturer supplied "IQ+" program to define operating parameters. IQ+ scans the available wavelength range using a series of 10 sub-scans that vary in terms of detector, radiant power, collimator crystal, and wavelength. While the instrument incorporates a sample rotation capability, this is not used by IQ+ since the time spent at any one wavelength is only a fraction of the pellet rotation time.

The channel mode is typically reserved for trace work. In this mode, the instrument moves to a specific wavelength and goniometer position and collects data for defined periods of time. These data collection periods are typically long enough to make use of the sample rotation function worth while. Other instrument operation parameters, such as tube power and crystal, are taken from the scan function parameters. The data collected in the channel mode is then incorporated into the sample's data file. The intent is to improve detection limits for certain trace elements that are often of interest at a small cost in analytical time.

Quantification is performed post-data collection using the program, "IQ+". IQ+ is a "first principles" quantification program that includes complex calculations to account for a wide variety of sample-specific parameters. For this reason, sample-specific calibrations are not necessary. This program calculates both peak heights and baseline values. The difference is then used, after adjustment by drift correction factors, for elemental quantification versus the calibration data. Interelement effects are possible and the software includes a library of such parameters. Data from secondary lines may be used for quantification where

interelement effects are significant or the primary peak is overloading the DAQ. Where the difference between the calculated peak height and baseline are of low quality, the program will not identify a peak and will not report results. IQ+ permits the inclusion of data from other sources by manual entry. Carbon is an example of this for these samples. Entry of other source data for elements indeterminable by XRF improves the mass balance.

5.2.5 XRF Detection Limits

Table 5-3 presents detection limit data in two forms, which are not mutually exclusive. The reporting limit is built into the software and reflects the manufacturer's willingness to report low-level data. Data listed under "detection limit" are based upon the short-term reproducibility of replicate analyses and are sample matrix specific. These calculations are likely to report higher detection limits for macro elements than what would be calculated where the same element is present at trace levels. In this data set, calcium is a likely example of this.

Table 5-3. XRF Reporting and Detection Limits

Analyte	Reporting Limit, µg/g	Detection Limit %, 2σ (wt. %)
Al	20	0.016
As	20	0.038
Ba	20	0.0084
Br	20	0.02
Ca	20	0.1
Cd	20	0.064
Ce	20	0.022
Cl	20	0.0046
Co	20	0.0024
Cr	20	0.0028
Cu	20	0.0014
F	20	0.082
Fe	20	0.034
Ga	20	0.0016
Ge	20	0.0014
K	20	0.0048
La	20	0.0054
Mg	20	0.01
Mn	20	0.0032
Mo	20	0.0026
Na	20	0.0076
Nb	20	0.0018
Ni	20	0.0048
Pb	20	0.0034
Px	20	0.004
Rb	20	0.0016
Sc	20	0.0016
Se	20	0.0018
Si	20	0.092
Sr	20	0.0016
Sx	20	0.05
Ti	20	0.003
V	20	0.0038
W	20	0.0036
Y	20	0.0018
Zn	20	0.0014
Zr	20	0.0024

5.2.6 Radionuclide Testing of CCRs using Ge-Detector

Fly ash, gypsum, and other CCRs were collected and assessed to determine their specific activity [Bq/kg]. Samples were taken from a variety of different sources to compare trends in radioactivity, such as that of bituminous and sub-bituminous CCRs. Samples will be analyzed using two High Purity Germanium (HPGe) photon detector with low energy detection capabilities, in a common geometry.

Detector 1: Ortec model GMX35P4 high purity germanium coaxial detector, 55.6 mm diameter, 79 mm length, 0.5 mm beryllium window, rated resolution 2.1 keV at 1332 keV, 31.5% relative efficiency at 1332 keV, GammaVision version 6.01 analytical software, 2003.

Detector 2: Canberra model BE3830 high purity germanium coaxial detector, 70 mm diameter, 30 mm length, 0.6 mm beryllium window, rated resolution 1.6 keV at 1332 keV, 27.9% relative efficiency at 1332 keV, Genie 2000 version 32.1 analytical software, 2009.

Project samples of fly ash and other coal combustion residues are received as dry materials and will be placed in plastic vials of approximately 250 ml and sealed to allow ingrowth of radon gas into equilibrium with its parent nuclide, as peaks from the radon progeny are key to identification of the parent nuclide. Sample containers are placed on the coaxial germanium photon detector systems and counted with shields closed. Traceable calibration standards in the same geometry had previously been counted on these systems to establish system calibrations. Samples are counted for times determined to be adequate to attain reasonable Minimum Detectable Activity (MDA) levels, 8 hours for fly ash and 12 hours for other residues. Results are given as values of activity per unit mass of sample, with associated uncertainties and MDA values. As MDAs are derived by pre-established regions on the gamma spectroscopy spectra which varies sample by sample, MDAs for a given nuclide on a particular system are slightly different for each sample but are generally consistent on a given detector for a stated geometry and count time. Fly ash samples are counted for 8 hrs, while all other samples are counted for 12 hr periods. The background characteristics of a number of photopeaks essential to the detection of U-238 and Th-232 decay series were determined over several weeks, and MDA levels were determined for each of the relevant regions.

The following photopeaks are used to determine activity in the U-238 decay series:

186 keV (Ra-226)
295 keV (Pb-214)
352 keV (Pb-214)
609 keV (Bi-214)
1754 keV (Bi-214)

The following photopeaks are used to determine activity in the Th-232 decay series:

583 keV (Tl-208)

911 keV (Ac-228)

Other photopeaks are evaluated regularly as naturally occurring peaks:

511 keV (various)

662 keV (Cs-137)

1460 keV (K-40)

6. Quality Assurance/Quality Control

6.1 Data Quality Indicator Goals

Data quality indicator (DQI) goals for critical measurements in terms of accuracy, precision and completeness are shown in Table 6-1. In addition, critical data quality indicator goals are inclusion of at least 6 independent laboratories in addition to the referee laboratory and 3 materials for each leaching test method evaluated.

These goals are based on past performance and will be assessed as the project is completed. Any deviations from these stated DQIs will be documented to the EPA WAM.

Table 6-1. Data Quality Indicator Goals

Measurement	Method	Accuracy	Precision	Completeness
ICP-OES constituents (e.g., As, B, Ba, Ca, Co, Cr, Mo, Sb, Se, V) Concentration	ICP-OES	±10%	±10%	>90%
pH, conductivity	Electrode	±2%	±2%	100%
Moisture	ASTM D2216-05	NA	±10%	100%
Hg	7470	±10%	±10%	90%
XRF	SOP No. 5003.3	±2%	±10%	100%
ICP/MS	6020	±10%	±10%	90%

NA = not applicable.

For the ICP-OES, accuracy is assessed using calibration verifications and laboratory control samples. Precision is assessed by replicate measurements. For the pH measurements, a standard of known pH will be checked prior to taking sample measurements. Precision is assessed by replicate measurements. There is not a standard reference material for moisture accuracy. Precision will again be assessed by replicate measurements.

In addition to the DQI goals shown in Table 6-1, homogeneity of the reference material will be considered acceptable if the following criteria are met by XRF. Major constituents are elements found at concentrations of more than 1%.

- RSD<10% for major constituents (greater than 1% total content)
- RSD<20% for minor constituents (greater than 0.1 to 1% total content)

- RSD<50% for trace constituents (less than 0.1 % total content).

Accuracy will be determined by calculating the percent bias from a known standard. Precision will be calculated as relative percent difference (RPD) between duplicate values and relative standard deviation (RSD) for parameters that have more than two replicates. Completeness is defined as the percentage of measurements that meet DQI goals of the total number measurements taken.

6.2 QC Sample Types

Types of QC samples used in this project will include blanks, spiked samples, replicates, and mass balance tests on the leaching reference material. For physical characterization testing, duplicate samples of the CCR leaching reference material will be processed through each analysis. The initial criteria will be determined on the screening data (the six replicates conducted by the ARCADIS referee laboratory) through a statistical review. This is done by looking at the leaching curves and bounding the data by the 5th and 95th percentiles as predicted by linear interpolations. The individual criteria will be determined by OCRC, ORD, Vanderbilt, and ARCADIS when they conduct this same statistical review on the data collected by each laboratory. As recommended by ORCR, each lab will be asked to have their extractions performed by a single operator on a single instrument in a single batch to minimize variability inherent to the determinative method; all leaching test eluates will be analyzed by ICP-OES for selected constituents by Vanderbilt to minimize variability associated with the metals analysis step since the focus of this study is on the leaching test methods not chemical analysis.

The EPA Metrology laboratory completes periodic and requested calibrations as described in SOPs and standard methods for equipment such as balances.

7. Data Reduction, Validation, and Reporting

7.1 Data Analysis

Interlaboratory comparisons of each method and material will be based on sets of analytes that are (i) representative of the range of characteristic behaviors anticipated for the material being tested and the test method being evaluated, and (ii) either analyzed as part of the laboratory procedure (e.g., pH) or analyzed as part of a single ICP-OES analytical method. Thus, it is anticipated that although some analytes will be common amongst different test materials being used in the interlaboratory comparisons, the complete set of analytes will likely be different for each test material because of different characteristic behaviors (e.g., as a function of pH and LS) and leaching concentrations relative to analytical detection limits. At least 6 analytes will be used as the basis for evaluation for each test material with priority given to analytes that are of regulatory interest and those that are major constituents of each test material. An initial set of analytes for each test material will be selected based on prior knowledge of the type of each test material selected (e.g., coal fly ash, cement stabilized waste, blast furnace slag). The final set of analytes for each test material will be selected based on the test method results obtained by the referee laboratory with the concurrence of the project team, including the EPA QA Representative, and prior to beginning analysis of samples from the participant laboratories.

The basis of the interlaboratory comparisons will be the dependent variables that are intended to be the information derived from each test procedure using the set of constituents selected for the test material being tested. The set of dependent variables for each test method are specified in the sub-sections that follow. The variance of the following additional analytes will be evaluated as reported by the referee laboratory and each participant laboratory to provide insights into material variability and methods implementation: moisture content, eluate pH, eluate conductivity.

Method 1313

The primary information to be derived from this test method is (i) the pH dependent leaching behavior of constituents of interest, and (ii) the pH titration curve of the material. The dependent variables that will serve as the basis for evaluation will be (i) material natural pH (as defined in the test method), (ii) eluate analyte concentration as determined for the method target pH values (i.e., 2.0, 4.0, 5.5, 7.0, 8.0, 9.0, 12.0, 13.0, natural pH, 10.5), and (iii) equivalents of acid or base required to be added to achieve the method target pH values (i.e., the pH titration curve). Variation in the actual pH about the target pH value of each eluate but within the tolerances specified in the test method will require interpolation or extrapolation of measured analyte concentration values to the precise target value. The initial method will be linear interpolation of the analyte concentration to the target pH value based on the log transform of the analyte concentration from the eluates having the nearest pH value greater than and less than the target value. If this method is found to provide poor representation of the overall pH dependent behavior of the analyte, then other interpolation

methods such as cubic splines or fifth-order polynomial fitting will be considered. The decision on the interpolation method will be based on the results obtained from the referee laboratory, prior to initiating evaluation of data from the participant laboratories. The same approach will be used for interpolation required to determine the equivalents of acid or base needed to be added to obtain the target eluate pH values. An ANOVA statistical evaluation (see below for ANOVA specification) will be used to evaluate the contributions to variance and method precision for the discrete values of the dependent variables at each target value of the appropriate independent variable.

An alternate method of data interpretation of the dependent variables will be based on the functional relationship of the dependent variable to the specified independent variable (i.e., analyte concentration as a function of pH or eluate pH as a function of acid or base addition). Thus, potential functional relationships (e.g., fifth order polynomials) will be regressed to the data set to provide a defined function to represent the overall result for each analyte. The contributions to variance in the resulting function then would serve as the basis for evaluating the method precision (see below for specification of statistical analysis of functional relationships).

Method 1314

The primary information to be derived from this test method is (i) the eluate pH and analyte concentration as a function of LS, and (ii) the cumulative release (i.e., mg of analyte per kg of material leached) of each analyte as a function of LS. The analyte concentration measured for eluates obtained at cumulative LS values of 0.2 and 0.5 can also be considered estimates of pore water composition and compared with similar estimates obtained from Method 1316. This interlaboratory comparison will be based on a complete characterization sampling scheme (Option A as specified in section 12.5.1.1 of the test method). The dependent variables that will serve as the basis for evaluation will be (i) eluate pH as determined at the method target LS values (i.e., 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, 10.0), (ii) eluate analyte concentration as determined at the method target LS values, and (iii) cumulative analyte release as determined at the method target LS values. Variation in the actual LS about the target LS value of each eluate but within the tolerances specified in the test method will require interpolation or extrapolation of measured analyte concentration values to the precise target value. The initial method of interpolation considered will be linear interpolation of the analyte concentration to the target LS value based on the log transform of the analyte concentration from the eluates having the nearest LS value greater than and less than the target value. If this method is found to provide poor representation of the overall LS dependent behavior of the analyte, then other interpolation methods such as cubic splines or exponential decay or error function curves will be considered. A common approach will be used for interpolation of eluate pH to the target LS values. The decision on the interpolation method to be used will be based on the results obtained from the referee laboratory and prior to initiating evaluation of data from the participant laboratories. An ANOVA statistical evaluation (see below for ANOVA specification) will be used to evaluate the contributions to variance and method precision for the discrete values of the dependent variables at each target value of the appropriate independent variable.

An alternate method of data interpretation of the dependent variables will be based on the functional relationship of the dependent variable to the specified independent variable (i.e., analyte concentration as a function of LS or cumulative release as a function of LS). Thus, potential functional relationships (e.g., exponential decay, error function or polynomial functions) will be regressed to the data set to provide a defined function to represent the overall result for each analyte. The contributions to variance in the resulting function then would serve as the basis for evaluating the method precision (see below for specification of statistical analysis of functional relationships).

Method 1315

The primary information to be derived from this test method is (i) the eluate pH and analyte flux as a function of time, (ii) the cumulative release (i.e., mg of analyte per m² of material leached based on the external geometric surface area of exposed faces) of each analyte as a function of time, and (iii) the mean observed diffusivity² of each analyte when diffusion controlled release is indicated (see Section 13.2 of Method 1315). The dependent variables that will serve as the basis for evaluation will be (i) eluate pH as determined at each method leaching interval (i.e., cumulative leaching times of 0.08, 1.0, 2.0, 7.0, 14.0, 28.0, 42.0, 49.0 and 63.0 days; see Table 1 of Method 1315), (ii) eluate analyte concentration as determined for each method leaching interval, (iii) cumulative analyte release for each leaching interval, (iv) analyte mean flux over each leaching interval, and (v) observed diffusivity for each analyte when applicable. Interpolation for determined concentrations and derived values of cumulative release and flux should not be necessary as long as leaching intervals are maintained within tolerances specified in the test method. An analysis of variance (ANOVA) statistical evaluation (see below) will be used to evaluate the contributions to variance and method precision for the discrete values of the dependent variables at each target value of the appropriate independent variable.

Method 1316

The primary information to be derived from this test method is (i) the eluate pH and analyte concentration as a function of LS, and (ii) the release (i.e., mg of analyte per kg of material leached) of each analyte as a function of LS. The dependent variables that will serve as the basis for evaluation will be (i) eluate pH as determined at the method target LS values (i.e., 0.5, 1.0, 2.0, 5.0, 10.0), (ii) eluate analyte concentration as determined at the method target LS values, (iii) analyte release as determined at the method target LS values, and (iv) an estimate of analyte concentration at LS value of 0.2 which can also be compared with the

² There will be up to 9 individual observations of observed diffusivity (one for each leaching interval¹) from each replicate of each application of Method 1315 for each specified analyte. Thus, a mean and standard deviation will be reported for each observed diffusivity value.

analyte concentration at LS value of 0.2 from Method 1314. Discrete values of each analyte are measured at each LS value and therefore interpolation will not be needed; however extrapolation of the functional relationship of analyte concentration as a function of LS will be needed to estimate the concentration at LS of 0.2. Extrapolation of analyte concentration as a function of LS to LS of 0.2 will be accomplished by regressing a functional relationship (e.g., linear, exponential or polynomial) to measured analyte concentrations in eluates from other LS values. Different functional relationships may be necessary for different analytes. The decision on the interpolation method to be used will be based on the results obtained from the referee laboratory and prior to initiating evaluation of data from the participant laboratories. An ANOVA statistical evaluation (see below) will be used to evaluate the contributions to variance and method precision for the discrete values of the dependent variables at each target value of the appropriate independent variable.

Statistical Analysis of Variance

The basic method of data analysis is provided as follows in the context of Method 1313 for a single analyte and a single material. The same approach will be used for Methods 1314, 1315 and 1316, as well as for multiple materials. It assumes that the interpolation to target measurement values (i.e., target pH values for Method 1313 and target LS values for Method 1314) has been performed and determined to be acceptable as described in the section titled "Outlier Identification and Model Assumption Checking." In the definitions given as follows, the convention is that a "measurement" refers to a log-transformed analyte concentration or other dependent variable value:

$Y_{i,j,k}$ = k^{th} measurement at the j^{th} target pH for the i^{th} lab,

where

$i = 1, \dots, M$ (M = number of labs in the study, where the reference lab is the M^{th}),

$j = 1, \dots, 9$ (the number of pH levels), and

$k = 1, 2, 3$ for participant labs 1 through $M - 1$; $k = 1, \dots, 6$ for the reference lab M

The statistical model underlying the analysis of variance is a mixed-effects model with fixed effects for pH level, and random effects for labs and lab-by-pH interactions. Specifically,

$$Y_{i,j,k} = \mu + \alpha_j + \beta_i + \gamma_{i,j} + \varepsilon_{i,j,k}$$

where

μ and α_j are fixed effects, to model the overall mean response at different pH levels,

β_i and $\gamma_{i,j}$ are random effects that model differences among labs, and

$\varepsilon_{i,j,k}$ is a random error term that models variation among replicates within a particular lab and pH combination.

The standard assumptions for the model are that β_i , $\gamma_{i,j}$ and $\varepsilon_{i,j,k}$ are independent normal random variables with zero means and variances σ_β^2 , σ_γ^2 , and σ^2 , respectively. The model will be fit to the data using appropriate routines in the established statistical software package, SAS.

Assessment of repeatability and reproducibility is made via the estimated variance components, with small values of estimated σ^2 indicating high repeatability, and small values of σ_β^2 and σ_γ^2 indicating high reproducibility.

Outlier Identification and Model Assumption Checking. The validity and utility of results from the statistical analysis depends on the assumptions underlying the statistical model and the integrity of the data. Thus the statistical analysis will be accompanied with an assessment of the suitability of the model and the data will be checked for aberrant values (outliers).

Checking the Interpolation. Because labs are not likely to precisely hit the target values, and because analyte concentrations might depend sensitively to the realized pH values, a preliminary assessment of the realized pH values and an assessment of the interpolation method to target pH values will be performed.

Assessing the Realized pH Values. Differences between the target and realized pH will be assessed for all labs at all target pH values. This will include summary analyses of the mean differences to determine whether there are systematic tendencies to under- or over-shoot the target values for different labs or target pH values and an assessment of variation of those differences to determine whether labs tend to be equally close to the target values. These analyses can be done using analysis of variance models similar to those described above, although the intent here is simply to quantify the performance of the labs at hitting the target values, for the purpose of justifying the interpolation step.

Assessing the Interpolation. The purpose of the interpolation step is to provide a common basis for comparing the measured values. It is anticipated that the interpolation will have little effect on the final data analysis, although this is something that will be checked. The most straightforward way to check the sensitivity of the interpolation step is to compare the statistical analysis results obtained using different

methods of interpolation, say via linear, polynomial, and spline curve fitting. If the results are sensitive to the calibration method, then it is anticipated that a spline method will supplant the proposed linear interpolation. The interpolation also introduces a secondary source of departure from the basic analysis of variance model assumptions in the form of dependence between the interpolated measurements. This can be assessed using advanced modeling features of Proc Mixed in SAS.

Outlier Identification. Possible outliers will be identified using standard methods of plotting residuals and comparing laboratory-specific summary measures of variability. It should be emphasized that in a study of this nature (interlaboratory study) there are multiple notions of what constitutes an "outlier" and these also manifest themselves as other forms of model violations. For example, the random error term in the statistical model is usually assumed to have the same variance at all pH levels where it is known that the variance is different at different pH levels (and is also assumed to be the same at all laboratories). This is directly checked by comparing between pH and within lab sample variances which can also be accomplished using advanced features of SAS's Proc Mixed procedure. A lab with a much greater variance than other those of other labs is a candidate for being declared an outlying lab. Regardless of how alleged outliers are identified, their impact on the statistical results is most definitively assessed by direct comparison of statistical results obtained via separate analyses using the full data set and the "cleaned" data set (with outliers removed).

More Advanced Modeling Options. For Method 1313, we are interpolating to the target pH values to have a consistent comparison of measured concentrations in eluates. Although this approach appears to work quite well for the fly ash data obtained so far, this may not prove to be the case with future materials. If this occurs, the approach would be changed to compare "curves" rather than individual values, thus changing to functional analysis (where "functional" refers to the types of curve fits used, such as polynomials). The basic idea is to fit a smooth curve to the analyte concentration as a function of pH (using the realized pH values) and then to compare the curves so obtained within labs (to assess repeatability) and among labs (to assess reproducibility). The basic methods and techniques of functional data analysis are described in the seminal book by Ramsay and Silverman (1997).

7.2 Chemical (ICP, XRF, AE-OES, OC/EC) and Physical (Moisture) Characterization

These data are reduced and reports are generated automatically by the instrument software or through spreadsheets. The primary analyst will review 100% of the report for completeness and to ensure that quality control checks meet established criteria. If QC checks do not meet acceptance criteria, sample analysis must be repeated. A secondary review will be performed by the Inorganic Laboratory Manager and Vanderbilt University to validate the analytical report. If appropriate, certain chemical characterization data will be compared to the XRF analyses. In addition, the ARCADIS QA Officer will review at least 10% of the raw data generated by ARCADIS for completeness. Analytical data will be summarized in periodic reports to the ARCADIS WAL. The procedures for reduction, validation and reporting of the leaching experiments (Task III) are outlined in the methods (<http://www.vanderbilt.edu/leaching/downloads.html>). ARCADIS WAL

is responsible for the implementation of these procedures. ARCADIS and Vanderbilt University will be responsible for publishing results and reports. QA/QC activities will be mentioned in any published materials. A data quality report will be provided in the final report of this investigation.

Data generated for the leachate analysis and total composition are entered into a standard Excel spreadsheet to ease uploading into the Vanderbilt metals database from the ICP-MS and other analyses. This data along with QA/QC information can be viewed using the "LeachXS Lite" software program developed by Vanderbilt University and the Energy Research Centre of the Netherlands. This software tool will allow users to view the metals leaching information based on sample type, facility configuration, or CCR coal type, or validation laboratory. This data viewer and database program will be available to the public on-line when complete. In addition, all data generated from the interlaboratory validation study will be archived by APPCD along with other project documentation.

7.3 Radionuclide Characterization

A Quality Assurance (QA) program involving verification of energy and Full Width at Half Maximum (FWHM) for several key photopeaks will be implemented. The calibration standard used to establish the system efficiency as a function of energy will be counted for 5 minutes daily. The photopeak energy, full width at half-maximum (FWHM) and net peak area for Cs-137 (662 keV) will be measured and plotted, with the FWHM for the 1332 keV peak of Co-60, for both detector systems. Any value occurring outside of 3 standard deviations of the mean (established in a preliminary study of about 20 measurements) must be immediately recounted. If the recount values are within 3 standard deviations, the system may be used for sample counting; if not an investigation into the detector reliability must be performed and a diagnosis and correction of any problems carried out before samples are counted on this system.

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8. Assessments

Assessments and audits are an integral part of a quality system. This project is assigned a QA Category III and, while desirable, does not require a planned technical systems audit (TSA). The ARCADIS QA Officer may conduct a TSA at the request of either the EPA WAM or the ARCADIS WAL. Internal assessments will be performed by project personnel to ensure acquired data meet data quality indicator goals established in Section 6.

There are currently no planned performance evaluation audits but Table 8-1 lists the measurement parameters and expected ranges should EPA determine a PEA should be provided.

Table 8-1. PEA Parameters and Ranges

Analyte or Measurement	Method	Expected Range
As, B, Ba, Ca, Co, Cr, Mo, Sb, Se, V	ICP-OES/3052/6020A	1-100 µg/mL
Hg	7470A	0.25 to 10 µg/L
pH	Electrode	0-14

The ARCADIS QA Officer will perform an internal data quality audit on at least 10% of the reported data. Reported results will be verified by performing calculations using raw data and information recorded in laboratory notebooks.

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9. References

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Appendix A

Participants in the Interlaboratory Study

Participant	Organization	Contact Information
James M. Tinjum	University of Wisconsin-Madison	James M. Tinjum, P.E., Ph.D. University of Wisconsin-Madison Department of Civil and Environmental Engineering 2214 Engineering Hall 1415 Engineering Drive Madison, WI 53706
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Charles Crawford	DOE- Savannah River National Laboratory	Charles L. Crawford Savannah River National Laboratory Bldg. 773-42A Savannah River Site Aiken, SC 29808 Needs to have an internal number attached to the box: PO# 0T0580
Hwidong Kim	University of Florida	Hwidong Kim 220 Black Hall Department of Environmental Engineering & Sciences University of Florida Gainesville, FL, 32611.
Johnny Mitchell	Test America (TVA)	Johnny Mitchell TestAmerica Laboratories – Nashville 2960 Foster Creighton Drive Nashville, TN 37204
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Jenet T. Hattaway	University of North Carolina Charlotte	Civil & Environmental Engineering University of North Carolina Charlotte Cameron Bldg. Rm 267 9201 University City Blvd. Charlotte, NC 28223-0002

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 DAG HD. AA D MAD DCHL A AO

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EC DC EA

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C B C C C

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1 C M C B B

C B B

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C B C 3 C B C

C B

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PRE METHOD 1213 LeachXS™ Lite Data Template

MOISTURE CONTENT (WET BASIS) AND SOLIDS CONTENT INSTRUCTIONS

Project	Code	Description () ()	Test conducted by: <input type="text"/>				
Material		: C					
Test Replicate		: C					

	Dish-1	Dish-2	Dish-3	Date	Time
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PreMethod 1313 LeachXS™ Lite Data Template

PRE-TEST TITRATION INSTRUCTIONS

Step 1: Enter the project, material and replicate codes as well as the technician name. In order to initiate test extraction setup, enter the maximum particle size, solids content, and reagent type and normality.

Step 2: Enter target acid or base additions from prior knowledge or from prediction of neutralization classifications in Draft Method 1313 Table 2 (note: base equivalents have a negative sign).

Step 3: Prepare five bottles, labelled P01 through P05, with solid material. Add reagent water and acid or base to the bottles according to the Schedule of Acid and Base Additions. Enter date and time that agitation of extracts begins.

Step 4: At the conclusion of the test, enter date and time that agitation ends. Record leachate pH. The pre-test titration curve for the material will be plotted automatically (note: axis adjustments may be necessary).

Step 5: From the pre-test titration, select the additions of acid and base required to complete the list of target pH (see Draft Method 1313 Table 5) plotted as horizontal blue dashed lines. These acid/base additions are to be entered into the "Test Data" sheet to create the Schedule of Acid and Base Additions.

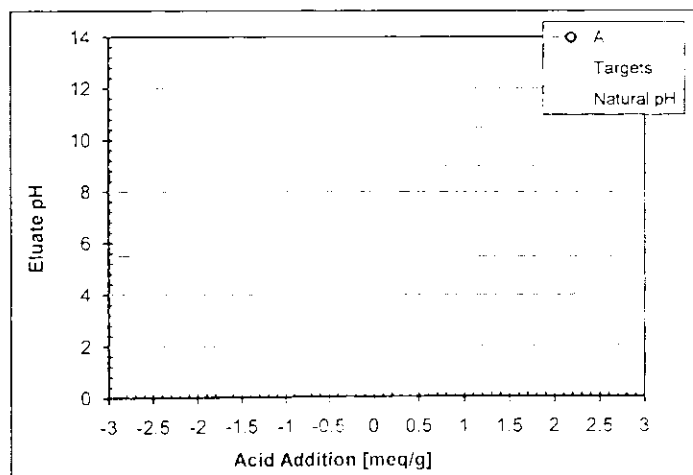
PreMethod 1313 LeachX3™ Lite Data Template

METHOD 1313 PRE-TEST TITRATION

Code		Description (optional)	Test conducted by:		Extraction Information	
Project		Auto-inserted from "Title Sheet"			LS Ratio	10 mL/g-dry
Material		Auto-inserted from "Title Sheet"			Liquid Volume / Extraction	200 mL
Test Replicate	A				Recommended Bottle Size *	250 mL
			Solids Information		Temperature	°C
			Particle Size (85 wt% less than)			mm
			Minimum Dry Equivalent Mass *			g-dry
			Solids Content (default = 1)			g-dry/g
			Mass of "As Tested" Material / Extraction			g
Date	Time					
Test Start						
Test End						
Required Contact Time *		[hr]	* Data based on Draft Method 1313 Table 1.			
Reagent Information						
Acid Type						
Acid Normality			meq/mL			
Base Type						
Base Normality			meq/mL			

Test Position	Schedule of Acid and Base Addition (±0.05)					additional extracts as needed				
	P01	P02	P03	P04	P05	P06	P07	P08	P09	P10
"As Tested" Solid [g] (±0.05g)	-	-	-	-	-	-	-	-	-	-
Reagent Water [mL] (±5%)	-	-	-	-	-	-	-	-	-	-
Acid Volume [mL] (±1%)	-	-	-	-	-	-	-	-	-	-
Base Volume [mL] (±1%)	-	-	-	-	-	-	-	-	-	-

Acid Addition [meq/g]										
Eluate pH										



Acid Addition

Required		
[meq/g-dry]	pH Target	Rationale
0		Natural pH at LS 10 mL/g-dry (no acid/base addition)
	2.0 ±0.5	Provides total or available content of COPCs
	4.0 ±0.5	Lower pH limit of typical management scenario
	5.5 ±0.5	Typical lower range of industrial waste landfills
	7.0 ±0.5	Neutral pH region; high release of oxyanions
	8.0 ±0.5	Endpoint pH of carbonated alkaline materials
	9.0 ±0.5	Minimum of LSP curve for many cationic and amphoteric COPCs
	12.0 ±0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
	13.0 ±0.5	Upper bound (field conditions) for amphoteric COPCs
	10.5 ±0.5	Substitution if natural pH falls within range of a mandatory pH target

49 4 7 6

6 98 7 8 98 93 6 A

Particle Size (85% less than) [mm]	US Sieve Size	Minimum Dry Equivalent [g-dry]	Contact Time [h]	Suggested Vessel Size [mL]
0.3	50	20±0.02	24±2	250
2	10	40±0.02	48±2	500
5	4	80±0.02	72±2	1000

6 98 4 6

Neutralization Classification	Acid or Base Addition [meq/g-dry]				
	P01	P02	P03	P04	P05
Low Alkalinity	-2	-1	0	1	2
Moderate Alkalinity	-2	0	2	5	10
High Alkalinity	0	5	10	15	25

Additional data points (e.g., T06, T07, T08 ...) may be needed to provide titration curve resolution

PRE METHOD 1313 LeachXSTM Lite Data Template

EXTRACTION TEST INSTRUCTIONS

Step 1: Enter the project, material and replicate codes as well as the technician name. To initiate test setup, enter the maximum particle size, solids content, and reagent type and normality.

Step 2: Enter target acid or base additions from prior knowledge or from the pre-test titration (note: base equivalents have a negative sign).

Step 3: Add solid material to nine bottles, labelled T01 through T09. Label an additional three bottles as blanks (B01, B02, and B03). Add DI water and acid or base to eleven bottles (i.e., T0x and B0x bottles) according to the Schedule of Acid and Base Additions. Enter date/time that extract agitation begins.

Note: If the acid or base is too dilute, large volume addition will be necessary. The acid or base normality may be adjusted for individual extractions.

Step 4: At the conclusion of the test, enter date and time that agitation ends. Record leachate information. Leachate pH and electrical conductivity (EC) will be plotted automatically (note: axis adjustments may be necessary).

Step 5: If the pH of the extract is within the target range and an analytical sample is to be saved, enter the letter "a" in the last row (font converts "a" to a check mark). If the extract will not be saved for chemical analysis, enter the letter "r" in the last row (font converts "r" to an X).

Code		Description (optional)	Test conducted by:	Extraction Information	
Project		Auto-inserted from "Title Sheet"		LS Ratio	10 mL/g-dry
Material		Auto-inserted from "Title Sheet"		Liquid Volume / Extraction	200 mL
Test Replicate	A			Recommended Bottle Size *	250 mL
			Solids Information		
			Maximum Particle Size		mm
			Minimum Dry Equivalent Mass *		g-dry
			Solids Content (default = 1)		g-dry/g
			Mass of "As Tested" Material / Extraction		g
			Neutered Reagent Information		
			Acid Type		
			Acid Normality		meq/mL
			Base Type		
			Base Normality		meq/mL

Enter "a" for "yes" or
"r" for "no".

PRE METHOD 1313 LeachAS™ Lite Data Template

METHOD 1313 EXTRACTION DATA

Project	Code	Description (optional)	Test conducted by:	Extraction Information	
Material		Auto-inserted from "Title Sheet"		LS Ratio	10 mL/g-dry
Test Replicate	B	Auto-inserted from "Title Sheet"		Liquid Volume / Extraction	200 mL
				Recommended Bottle Size *	250 mL
				Temperature	°C
				Solids Information	
			Maximum Particle Size		mm
			Minimum Dry Equivalent Mass *		g-dry
			Solids Content (default = 1)		g-dry/g
			Mass of "As Tested" Material / Extraction		g
				Nominal Reagent Information	
				Acid Type	
				Acid Normality	meq/mL
				Base Type	
				Base Normality	meq/mL

Date Time
 Test Start
 Test End
 Required Contact Time * hr

* Data based on Draft Method 1313 Table 1.

Schedule of Acid and Base Addition

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03	totals
"As Tested" Solid [g] ($\pm 0.05g$)	-	-	-	-	-	-	-	-	-	no solid	no solid	no solid	g
Reagent Water [mL] ($\pm 5\%$)	-	-	-	-	-	-	-	-	-	-	-	-	mL
Acid Volume [mL] ($\pm 1\%$)	-	-	-	-	-	-	-	-	-	-	-	-	mL
Base Volume [mL] ($\pm 1\%$)	-	-	-	-	-	-	-	-	-	-	-	-	mL
Acid Normality [meq/mL]	-	-	-	-	-	-	-	-	-	-	-	-	
Base Normality [meq/mL]	-	-	-	-	-	-	-	-	-	-	-	-	
Target pH	13.0 \pm 0.5	12.0 \pm 0.5	10.5 \pm 0.5	9.0 \pm 0.5	8.0 \pm 0.5	7.0 \pm 0.5	5.5 \pm 0.5	4.0 \pm 0.5	2.0 \pm 0.5				
Acid Addition [meq/g]										Water	Acid	Base	
Eluate pH													
Eluate EC [mS/cm]													
Eluate Eh [mV]													
Save? (enter "a" or "r")													
Notes													

Note: If multiple replicate tests are carried out in parallel, only one set of method blanks is necessary.

PRE-METHOD 1313 - LeachX5™ Lite Data Template

METHOD 1313 EXTRACTION DATA

	Code	Description (optional)	Test conducted by:
Project	<input type="text"/>	Auto-inserted from "Title Sheet"	<input type="text"/>
Material	<input type="text"/>	Auto-inserted from "Title Sheet"	
Test Replicate	<input type="text" value="C"/>		

Solids Information	
Maximum Particle Size	<input type="text"/> mm
Minimum Dry Equivalent Mass *	<input type="text"/> g-dry
Solids Content (default = 1)	<input type="text"/> g-dry/g
Mass of "As Tested" Material / Extraction	<input type="text"/> g

Extraction Information		
LS Ratio	<input type="text" value="10"/>	mL/g-dry
Liquid Volume / Extraction	<input type="text" value="200"/>	mL
Recommended Bottle Size *	<input type="text" value="250"/>	mL
Temperature	<input type="text" value="21"/>	°C

Date	<input type="text"/>	Time	<input type="text"/>
Test Start	<input type="text"/>		
Test End	<input type="text"/>		

Required Contact Time * hr

* Data based on Draft Method 1313 Table 1.

Nominal Reagent Information	
Acid Type	<input type="text"/>
Acid Normality	<input type="text"/> meq/mL
Base Type	<input type="text"/>
Base Normality	<input type="text"/> meq/mL

Schedule of Acid and Base Addition

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03	totals
"As Tested" Solid [g] (±0.05g)	-	-	-	-	-	-	-	-	-	no solid	no solid	no solid	g
Reagent Water [mL] (±5%)	-	-	-	-	-	-	-	-	-	-	-	-	mL
Acid Volume [mL] (±1%)	-	-	-	-	-	-	-	-	-	-	-	-	mL
Base Volume [mL] (±1%)	-	-	-	-	-	-	-	-	-	-	-	-	mL
Acid Normality [meq/mL]	-	-	-	-	-	-	-	-	-	-	-	-	
Base Normality [meq/mL]	-	-	-	-	-	-	-	-	-	-	-	-	

Target pH	13.0±0.5	12.0±0.5	10.5±0.5	9.0±0.5	8.0±0.5	7.0±0.5	5.5±0.5	4.0±0.5	2.0±0.5	Water	Acid	Base
Acid Addition [meq/g]												
Eluate pH												
Eluate EC [mS/cm]												
Eluate Eh [mV]												
Save? (enter "a" or "r")												
Notes												

Note: If multiple replicate tests are carried out in parallel, only one set of method blanks is necessary.

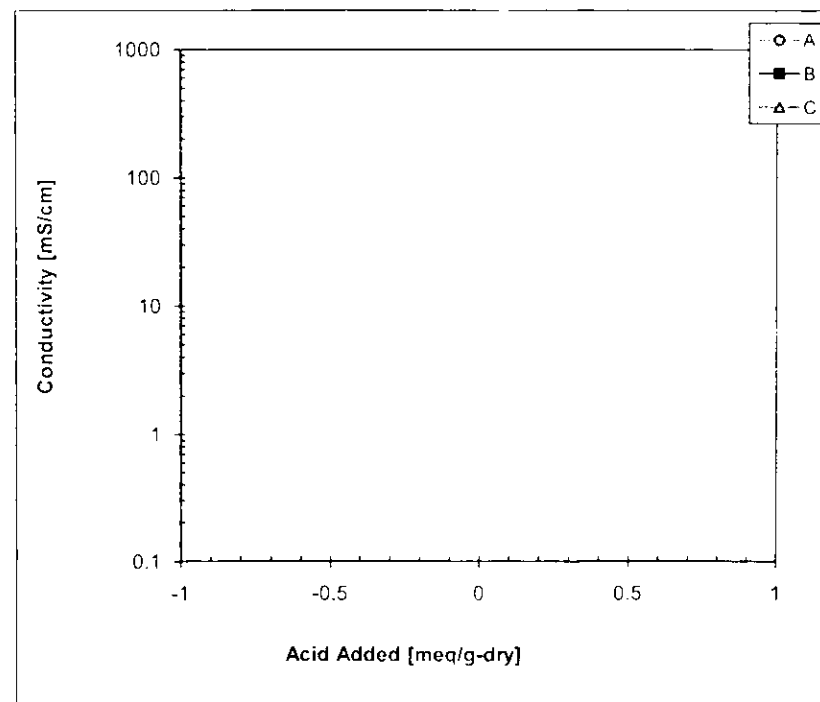
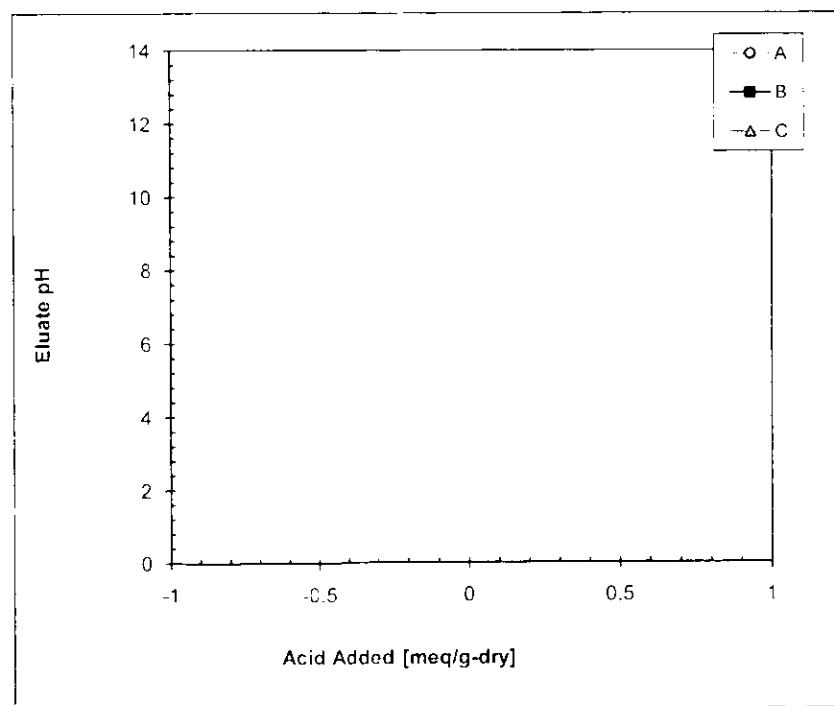
PRE METHOD 1313 LeachXS™ Lite Data Template

Table 4 Extraction Parameters as a Function of Particle Size

Maximum Particle Size [mm]	US Sieve Size	Minimum Dry Equivalent [g-dry]	Contact Time [h]	Suggested Vessel Size [mL]
0.3	50	20±0.02	24±2	250
2	10	40±0.02	48±2	500
5	4	80±0.02	72±2	1000

Table 5 Final Extract pH Targets

pH Target	Rationale
varies	Natural pH at LS 10 mL/g-dry (no acid/base addition)
2.0±0.5	Provides total or available COPC content
4.0±0.5	Lower pH limit of typical management scenario
5.5±0.5	Typical lower range of industrial waste landfills
7.0±0.5	Neutral pH region; high release of oxyanions
8.0±0.5	Endpoint for carbonated alkaline materials
9.0±0.5	Minimum of LSP curve for many cationic and amphoteric COPCs
12.0±0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
13.0±0.5	Upper bound (field conditions) for amphoteric COPCs
10.5±0.5	Substitution if natural pH falls within another mandatory target



6 " " 45 2 4 4 4

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This page is for selection of a final set of nine extractions per test replicate from the "Lab Extractions" data. All data is manually input by the user based on if extraction meet the pH criteria.

Interlaboratory Validation of LEAF Method 1313 and Method 1316

METHOD 1313 SELECTED ANALYTICAL SOLUTIONS

Code Description (optional)

Project Auto-inserted from "Title Sheet"

Material Auto-inserted from "Title Sheet"

Test Replicate A

Max Particle Size mm

Solids Content g-dry/g

Temperature °C

Acid Type selected from drop-down menu

Base Type selected from drop-down menu

Lab Technician

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03
Test Start Date												
Extraction Duration [hr]												
"As Tested" Solid [g]												
Reagent Water [mL]												
Acid Volume [mL]												
Base Volume [mL]												
Acid Normality [meq/mL]												
Base Normality [meq/mL]												
Acid Addition [meq/g]										Water	Acid	Base
Eluate pH												
Eluate EC [mS/cm]												
Eluate Eh [mV]												
Remarks												

Test Replicate B

Max Particle Size mm

Solids Content g-dry/g

Temperature °C

Acid Type selected from drop-down menu

Base Type selected from drop-down menu

Lab Technician

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03
Test Start Date												
Extraction Duration [hr]												
"As Tested" Solid [g]												
Reagent Water [mL]												
Acid Volume [mL]												
Base Volume [mL]												
Acid Normality [meq/mL]												
Base Normality [meq/mL]												
Acid Addition [meq/g]										Water	Acid	Base
Eluate pH												
Eluate EC [mS/cm]												
Eluate Eh [mV]												
Remarks												

Test Replicate C

Max Particle Size mm

Solids Content g-dry/g

Temperature °C

Acid Type selected from drop-down menu

Base Type selected from drop-down menu

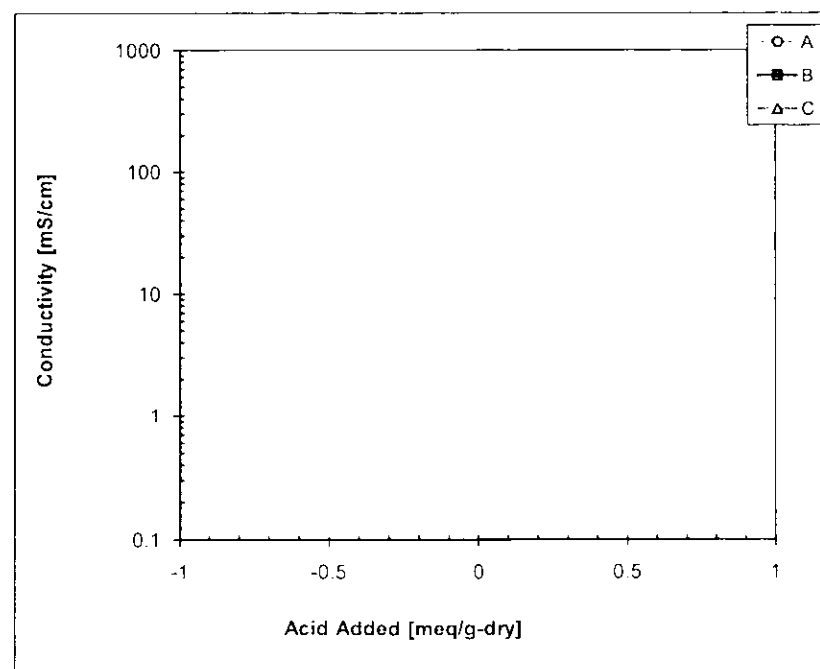
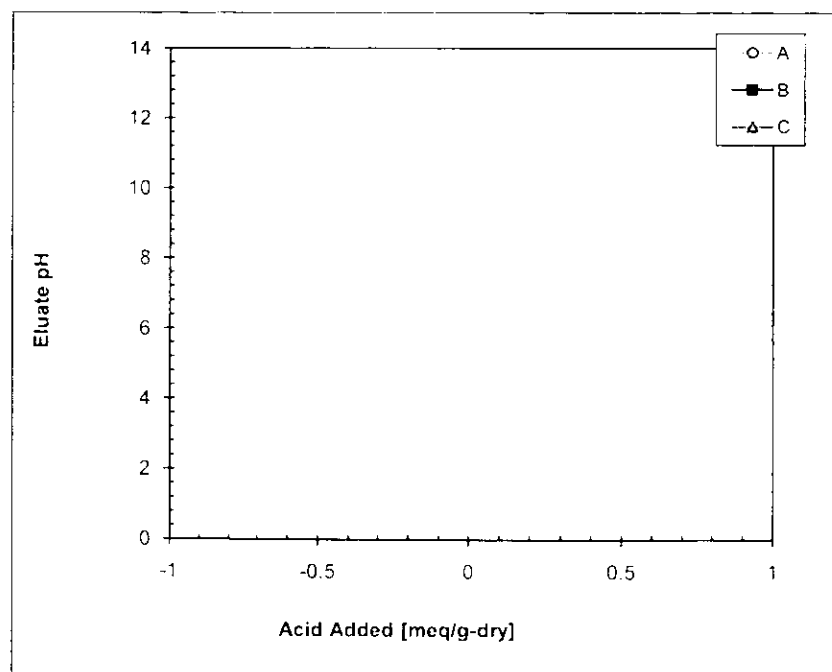
Lab Technician

Test Position	T01	T02	T03	T04	T05	T06	T07	T08	T09	B01	B02	B03
Test Start Date												
Extraction Duration [hr]												
"As Tested" Solid [g]												
Reagent Water [mL]												
Acid Volume [mL]												
Base Volume [mL]												
Acid Normality [meq/mL]												
Base Normality [meq/mL]												
Acid Addition [meq/g]										Water	Acid	Base
Eluate pH												
Eluate EC [mS/cm]												
Eluate Eh [mV]												
Remarks												

Pre-Method 1316, Version 3.0™ Lite Data Template

Table 5 Final Extract pH Targets

pH Target	Rationale
varies	Natural pH at LS 10 mL/g-dry (no acid/base addition)
2.0±0.5	Provides total or available COPC content
4.0±0.5	Lower pH limit of typical management scenario
5.5±0.5	Typical lower range of industrial waste landfills
7.0±0.5	Neutral pH region; high release of oxyanions
8.0±0.5	Endpoint for carbonated alkaline materials
9.0±0.5	Minimum of LSP curve for many cationic and amphoteric COPCs
12.0±0.5	Maximum in alkaline range for LSP curves of amphoteric COPCs
13.0±0.5	Upper bound (field conditions) for amphoteric COPCs
10.5±0.5	Substitution if natural pH falls within another mandatory target



Interlaboratory Validation of LEAF Method 1313 and Method 1316

PreMethod 1313 LeachXS™ Data Template

METHOD 1313 MASTER DATA LIST

Project ID:
 Material ID:
 Test ID:

Code:
 Description (optional):
 Auto-inserted from "Title Sheet"
 Auto-inserted from "Title Sheet"

Test Rep A:
 Test Rep B:
 Test Rep C:

QC Flags:
 J Value greater than calibration
 E Value between MDL and ML
 U Value less than MDL
 U1/2 Value less than MDL (shown at 1/2 MDL)

MDL

ML

Analysis Method

Analysis Date

Analytical Lab Name

Eluate Composition

Sample ID	"As Tested" Solids g	Moisture Content g-H ₂ O/g	Water Added mL	Acid Added mL	Acid Strength N	Base Added mL	Base Strength N	Acid Added meq/g-dry	Eluate pH s.u.	Eluate Conductivity mS/cm	Eluate ORP mV
-1313-T01-A											
-1313-T02-A											
-1313-T03-A											
-1313-T04-A											
-1313-T05-A											
-1313-T06-A											
-1313-T07-A											
-1313-T08-A											
-1313-T09-A											
-1313-T01-B											
-1313-T02-B											
-1313-T03-B											
-1313-T04-B											
-1313-T05-B											
-1313-T06-B											
-1313-T07-B											
-1313-T08-B											
-1313-T09-B											
-1313-T01-C											
-1313-T02-C											
-1313-T03-C											
-1313-T04-C											
-1313-T05-C											
-1313-T06-C											
-1313-T07-C											
-1313-T08-C											
-1313-T09-C											
-1313-B01-A	-	-						-			
-1313-B02-A	-	-						-			
-1313-B03-A	-	-						-			

Post-Method 1313 LeachX5™ Data Table (cont.)

PreMethod 1316 LeachX5™ L-1 Data Table (cont.)

Detection and Quantification Limits

Al	As	B	Bi	Br	C	Ca	Co	Cr	Cu	Fe	Mn	Mo	Ni	P	Pb	S	Sb	Se	Si	Sn	Ti	V	Zn

--

1		2		3		4		5		6		7		8		9		10		11		12	
Aluminum Al μg/L	QC	Antimony Sb μg/L	QC	Arsenic As μg/L	QC	Bismuth Bi μg/L	QC	Boron B μg/L	QC	Cadmium Cd μg/L	QC	Calcium Ca μg/L	QC	Cerium Ce μg/L	QC	Chromium Cr μg/L	QC	Cobalt Co μg/L	QC	Copper Cu μg/L	QC		

PreMethod 1313 LeachXS™ Lite Data Template

Pb	Pb	Li	Mg	Mn	Mo	Ni	P	K	Se	Si	Na

13		14		15		16		17		18		19		20		21		22		23		24	
Iron Fe µg/L	QC	Lead Pb µg/L	QC	Lithium Li µg/L	QC	Magnesium Mg µg/L	QC	Manganese Mn µg/L	QC	Molybdenum Mo µg/L	QC	Nickel Ni µg/L	QC	Phosphorus P µg/L	QC	Potassium K µg/L	QC	Selenium Se µg/L	QC	Silicon Si µg/L	QC	Sodium Na µg/L	QC

Interlaboratory Validation of LEAF Method 1313 and Method 1316

Product Model 1313 LeachXS™ Lite Data Template

Str	S	Tl	Sr	U	V	Co	Hg	Pb	As	NO ₂

25	Strontium Sr µg/L	26	Sulfur S µg/L	27	Thallium Tl µg/L	28	Tin Sn µg/L	29	Titanium Ti µg/L	30	Uranium U µg/L	31	Vanadium V µg/L	32	Zinc Zn µg/L	33	Mercury Hg µg/L	34	Fluoride F µg/L	35	Chloride Cl µg/L	36	Nitrite NO2 µg/L
	QC		QC		QC		QC		QC		QC		QC		QC		QC		QC		QC		QC

Interlaboratory Validation of LEAF Method 1313 and Method 1316

Br	NO3	SO4	PO4	DIC	DOC	NH3

37	38	39	40	41	42	43
Bromide Br µg/L	Nitrate NO3 µg/L	Sulfate SO4 µg/L	Phosphate PO4 µg/L	Inorganic C DIC µg/L	Organic C DOC µg/L	Ammonia NH3 µg/L



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Office of Research and Development
Environmental Systems Laboratory
U.S. Environmental Protection Agency
Washington, D.C. 20460

Dear Leach Validation Participant,

Welcome to the Phase I validation of PreMethods 1313 (pH dependent leach test) and 1316 (L/S ratio leach test). These methods represent a significant step forward in the science of modeling material leaching into the environment. As a participatory laboratory, your assistance in this effort will help ensure these methods are incorporated in EPA's publicly available method compendium *Test Methods for Evaluating Solid Waste Physical/Chemical Methods* (SW-846).

As you review the methods, along with the instructions and materials enclosed in this package, I would like to highlight a couple of key points. First, please make sure you download and review the most current version of PreMethods 1313 and 1316 along with the laboratory instruction sheet (enclosed) before running the methods (see www.vanderbilt.edu/leaching). Some minor changes and clarifications were recently made to the methods to help improve their usability. Second, please check the list of materials provided on the instruction sheet to ensure your kit is complete. Lastly, please note that since you will be shipping the extracted elluates to Vanderbilt University for analysis, it is important that you follow the preservation instructions to ensure accurate results.

From the start of this interlaboratory validation effort, one of our top priorities is to make sure we are being responsive to the needs of our participating labs. As such, please do not hesitate to contact me with any problem, issue, or concern you may have throughout this process. You can contact me by phone at 703-308-0157 or by email at baldwin.mark@epa.gov. Again on behalf of the EPA, I would like to thank you and your laboratory for your invaluable contribution to this validation effort.

Sincerely,

A handwritten signature in black ink, appearing to read "Mark Baldwin".

Mark Baldwin

Phase I of Method 1313/Method 1316 Validation

The subject material for Phase I of the Method 1313/Method 1316 inter-laboratory validation study is a coal combustion fly ash. A generic MSDS for coal fly ash is included with the material shipment.

The subject material may be treated as a well homogenized sample with 85% < 0.3 mm particle size. Thus:

- the minimum equivalent dry mass for Method 1313 and Method 1316 will be 20 g-dry and all extractions may be conducted in 250-mL bottles with the exception of two low liquid-solid (L/S) ratio test positions, 1316-T04 and T05, which will likely require higher amounts of solid materials in a 500 mL bottles in order to ensure 50 mL analytical solutions
- no particle size reduction or sieve analysis is required for this Phase I sample

Although the titration curve should be developed as part of the method validation, baseline characterization has shown the titration curve for the Phase I material to be very sensitive to acid addition in the neutral range. Extreme care should be taken to provide exact volumes of acid addition during (i) the pre-test titration in order to produce an accurate titration curve and (ii) the extraction step in order to reproduce an acceptable final pH. Test positions that meet pH tolerances should be processed for chemical analysis and only those test positions that do not meet test position pH tolerances need to be rerun.

The kit supplied for the Phase I validation study includes:

- Four sets of completed bottle labels for each test replicate
- One chain of custody form
- Two questionnaires (one for each Method 1313 and Method 1316)

The sample labeling convention used to identify a particular solution consists of numerical identifiers for the material, lab, test method, and test position along with an alphabetical identifier for the test replicate. The layout for the sample label convention is as follows:

MaadLbb-131c-Tdd-e (Test Positions T01 through T09)

MaadLbb-131c-Bdd-e (QA/QC Blanks B01-B03)

“aa” is a two-digit number starting at zero that identifies the test material (e.g., the Phase I material is M01).

“bb” is a two-digit number starting at zero that identifies the participating laboratory (assigned randomly by EPA-ORCR).

“c” is a single digit number that completes the test method ID (i.e., 1313 or 1316).

“dd” is a two-digit number starting at zero that identifies the test position or QA/QC blank.

“e” is a single letter representing the test replicate (i.e., A, B or C).

Four sets of completed labels are provided to be used for labeling extraction vessels and two sets of 50-mL analytical samples. The remaining fourth set may be reserved for replacements as needed.

Instructions for Phase I Validation

On or before June 7, 2010:

1. Prepare 3 test replicates of extracts for the supplied sample material according to the most current versions of Method 1313 and Method 1316¹. Use the Excel data templates to calculate extract "recipes" and return a completed Excel data template to the Vanderbilt project lead, Andy Garrabrants (A.Garrabrants@vanderbilt.edu) via email. Each method should be conducted as specified in the method draft to the extent possible; however, any necessary deviations should be recorded and a log of deviations returned with the Excel data template.
2. For each test position and QA/QC blank, collect two 50-mL analytical samples in the DigiTubes provided. Preserve each analytical sample with Optima grade (or similar purity) nitric acid to a final concentration of 1% (v/v). Each analytical sample should have a label (prefilled and provided) corresponding to its test position (e.g., T01-T09) and test replicate (e.g., A, B, and C).
3. Return one set test positions and QA/QC blanks in 50-mL DigiTubes for each Method 1313 and Method 1316 to Vanderbilt University for chemical analysis and retain the remaining set of samples onsite at least until the end of Phase I testing.

Shipments should be sent no later than June 7, 2010 and a completed chain of custody form (provided) should be included. Please ship samples (Monday through Thursday pickup only as Vanderbilt cannot accept Saturday deliveries) to following address:

Civil & Environmental Engineering
Vanderbilt University
c/o Rossane DeLapp
Jacobs Hall 149
400 24th Avenue South
Nashville, TN 37235
(615) 322-3189

Please inform the ORCR study lead, Mark Baldwin (Baldwin.Mark@epa.gov), and Vanderbilt lead, Andy Garrabrants (A.Garrabrants@vanderbilt.edu), of your intended ship date so that arrangements may be made to receive the shipment.

4. Complete the method feedback questionnaire for each test method (available at www.vanderbilt.edu/teaching/downloads.html) and return it to Mark Baldwin by email no later than June 7, 2010.

Programmatic and technical questions may be directed to the ORCR lead, Mark Baldwin (Baldwin.Mark@epa.gov, 703-308-0157).

¹ The latest versions of these test methods and data templates may be downloaded at www.vanderbilt.edu/teaching/downloads.html. Although the procedures themselves are not changed in any way, the method drafts dated April 26, 2010 contain minor clarifications to the method which are intended to improve understanding of the method

M01-L01-1313-T01-A	M01-L01-1313-T01-B	M01-L01-1313-T01-C
M01-L01-1313-T02-A	M01-L01-1313-T02-B	M01-L01-1313-T02-C
M01-L01-1313-T03-A	M01-L01-1313-T03-B	M01-L01-1313-T03-C
M01-L01-1313-T04-A	M01-L01-1313-T04-B	M01-L01-1313-T04-C
M01-L01-1313-T05-A	M01-L01-1313-T05-B	M01-L01-1313-T05-C
M01-L01-1313-T06-A	M01-L01-1313-T06-B	M01-L01-1313-T06-C
M01-L01-1313-T07-A	M01-L01-1313-T07-B	M01-L01-1313-T07-C
M01-L01-1313-T08-A	M01-L01-1313-T08-B	M01-L01-1313-T08-C
M01-L01-1313-T09-A	M01-L01-1313-T09-B	M01-L01-1313-T09-C
M01-L01-1313-B01-A	M01-L01-1313-B01-B	M01-L01-1313-B01-C

Method Feedback Questionnaire

METHOD 1313: Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Procedure

1. Please indicate the amount of time (in professional hours) required to complete the following steps of Method 1313:

Material Preparation (e.g., air drying, particle-size reduction, sieving) _____ hrs

Pre-test Titration _____ hrs

Extraction Setup (e.g., solids, water, acid/base additions) _____ hrs

Eluate Processing (e.g., pH/cond. filtration, analytical prep) _____ hrs

2. How would you rate the overall usability of Method 1313?

3. In total, how much time (in professional hours) was required to process three test replicates of the test material using Method 1313?

4. Were the overall goals and instructions provided with the sample material clearly laid out and easy to follow? If not, please suggest specific sections of the method where clarifications could be made.

5. Were the procedures in the method draft clearly laid out and easy to follow? If not, please suggest specific sections of the method where clarifications could be made.

6. Was the Excel data template clearly laid out and easy to follow? If not, please suggest specific sections of the data template where clarifications could be made.

7. In preparing solid samples for the method, what difficulties (if any) were encountered? How were these difficulties overcome?

8. While defining the pre-test titration curve, what difficulties (if any) were encountered? How were these difficulties overcome?

9. When using the Excel data template sheets, what difficulties (if any) were encountered? How were these difficulties overcome?

10. What difficulties (if any) did you encounter with acquiring or operating the required equipment?

[illegible]

11. How much time did it take technical personnel to become familiar with the method?

12. Please provide any general feedback (e.g., comments, edits, questions, software glitches, or concerns) below. Include any suggested modifications to the test procedure, the Excel data template or to the method draft.

[illegible]

Method Feedback Questionnaire

METHOD 1316: Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio using a Parallel Batch Procedure

1. Please indicate the amount of time (in professional hours) required to complete the following steps of Method 1316:

Material Preparation (e.g., air drying, particle-size reduction, sieving) _____ hrs

Extraction Setup (e.g., solids, water, acid/base additions) _____ hrs

Eluate Processing (e.g., pH/cond, filtration, analytical prep) _____ hrs

2. How would you rate the overall usability of Method 1316?

3. In total, how much time (in professional hours) was required to process three test replicates of the test material using Method 1316?

4. Were the overall goals and instructions provided with the sample material clearly laid out and easy to follow? If not, please suggest specific sections of the method where clarifications could be made.

5. Were the procedures in the method draft clearly laid out and easy to follow? If not, please suggest specific sections of the method where clarifications could be made.

6. Was the Excel data template clearly laid out and easy to follow? If not, please suggest specific sections of the data template where clarifications could be made.

7. In preparing solid samples for the method, what difficulties (if any) were encountered? How were these difficulties overcome?

8. When using the Excel data template sheets, what difficulties (if any) were encountered? How were these difficulties overcome?

9. What difficulties (if any) did you encounter with acquiring or operating the required equipment?

10. How much time did it take technical personnel to become familiar with the method?

11. Please provide any general feedback (e.g., comments, edits, questions, software glitches, or concerns) below. Include any suggested modifications to the test procedure, the Excel data template or to the method draft.

[illegible]

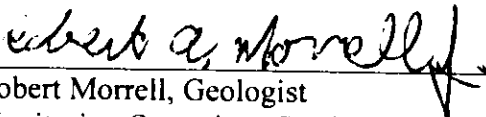
RCRA SAMPLING QA PROJECT PLAN
AES GUAYAMA

Guayama, Puerto Rico

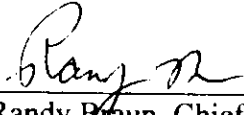
Responsible Agency: U.S. Environmental Protection Agency
Monitoring and Assessment Branch

Requesting Agency: U.S. Environmental Protection Agency
RCRA Compliance Branch

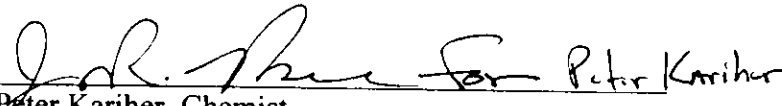
Project Officer:


Robert Morrell, Geologist
Monitoring Operations Section

Quality Assurance Officer:

 3/1/12
Randy Braun, Chief
Monitoring Operations Section

Laboratory Coordinator:


Peter Kariher, Chemist
USEPA-RTP

1. **Project Name:** RCRA Sampling Investigation
AES Guayama
2. **Project Requested By:** Leonard Grossman, Enforcement Officer
RCRA Senior Enforcement Team
3. **Date of Request:** February 3, 2012
4. **Date of Project Initiation:** February 21, 2012
5. **Project Officer:** Robert Morrell, Geologist
Monitoring Operations Section
6. **Quality Assurance Officer:** Randy Braun, Chief
Monitoring Operations Section
7. **Project Description:**
 - a. **Introduction and Site Background:** AES Guayama is a coal-fired electrical power plant located on Route 3 in Guayama, Puerto Rico. During the combustion of coal, fly ash and bottom ash are generated. Agremax has been contracted by AES Guayama to explore beneficial uses for the coal combustion products. Fly ash and bottom ash are mixed with water to produce a manufactured aggregate, which gains strength with time, similar to cement. After curing, the manufactured aggregate is crushed to gravel-size. Agremax intends to use the manufactured aggregate for applications such as road beds, soil amendments, asphalt, and concrete. EPA is currently developing a Leaching Environmental Assessment Framework (LEAF), which consists of four leaching methods that are designed to characterize materials intended for beneficial reuse. A representative sample of the manufactured aggregate was requested by the RCRA Compliance Branch to assist in the development of the four proposed leaching methods.
 - b. **Objective and Scope of Work:** The purpose of this sampling survey is to collect a representative composite sample from piles of the manufactured aggregate that are being stored on the AES Guayama facility. This sample will be used to develop leaching methods that can be used to characterize materials such as coal combustion products. The analytical results will provide a leaching assessment of the TCLP metals.
8. **Tentative Schedule of Tasks and Products:**

Project Assigned:	February 3, 2012
Development of QAPP:	February 29, 2012
QAPP Submitted for Approval:	March 1, 2012
Equipment Preparation:	March 2, 2012

Field Work:	March 13, 2012
Sample Chain-of-Custody Relinquished to Lab:	March 14, 2012
Laboratory Report Completed:	April 16, 2012
Final Report Completed:	May 16, 2012

9. **Project Organization and Responsibility:**

The following is a list of key project personnel and their corresponding responsibilities for samples analyzed at the U.S. EPA RTP Laboratory:

Robert Morrell.....	Sampling Operations
Randy Braun.....	Sampling QC
Peter Kariher.....	Laboratory Sample Coordinator
Peter Kariher.....	Data Processing
Randy Braun.....	Quality Assurance Officer
Robert Morrell.....	Overall Project Coordinator

10. **Data Quality Requirements:**

For samples analyzed by the U.S. EPA RTP Laboratory, the data must, at a minimum, conform to the Laboratory QA/QC Plans, as prepared by the RTP Laboratory.

Sample Representativeness: Sample containers, sampling equipment, sample collection techniques, and chain of custody procedures will conform with standard EPA Region 2 protocol.

All precleaned sample containers and glassware for chemical analysis will be provided by Environmental Sampling Supply (ESS). Quality assurance documentation of sample container cleanliness will be provided by ESS, if requested.

11. **Sampling Procedures:**

A polypropylene scoop will be used to collect a composite sample of the piles of manufactured aggregate being stored on the AES Guayama facility. The composite sample will be mixed in a 5-gallon plastic bucket. After mixing, the material will be transferred to 2-liter plastic jars. The composite sample will be analyzed for TCLP metals using the four methods outlined in LEAF.

The methods employed will follow DESA sampling protocols and the equipment will be constructed of inert materials to prevent contamination. If any deviations from established procedures are used, they will be documented in the field notebook. All samples will be analyzed at the U.S. EPA RTP Laboratory in Durham, North Carolina.

12. **Calibration Procedures and Preventative Maintenance:**

- a. Field Equipment: All field equipment will be prepared and calibrated prior to the sampling survey using instruction manuals provided with the equipment.
- b. Laboratory Equipment: Laboratory instrumentation is calibrated to meet method-specified tuning and/or calibration criteria and maintained in accordance with the manufacturer's specifications and EPA QA/QC procedures.

13. **Documentation, Data Reduction, and Reporting:**

- a. Documentation: All written notes and sample logs will be recorded in a bound field notebook. Chain of Custody / Field Data Forms and sample labels will be prepared by field personnel and given to the laboratory with the samples. The Monitoring and Assessment Branch will retain all field notes and photographs. The RTP Laboratory will maintain QA/QC records.
- b. Data Reduction and Reporting: Data will be reported by the EPA RTP laboratory in LIMS designated units.

14. **Data Validation:**

Data will be validated by the procedures outlined in the SOP's prepared by the EPA RTP Laboratory.

15. **Performance and System Audits:**

System audits are conducted on a continual basis at the EPA RTP laboratory.

16. **Laboratory and Field Corrective Action:**

Appropriate methods are followed to detect and correct problems, e.g. audits and equipment blanks. Any biological and chemical tests that do not adhere to analytical QA/QC criteria will be retested and reanalyzed. If certain criteria are still exceeded in second testing, then appropriate qualifiers will be added.

17. **Reports:**

Upon receipt of QA/QC validated data from the EPA RTP laboratory, a written report will be drafted for review and finalized for signature within 30 working days. The report will be sent to the RCRA Compliance Branch.

PARAMETER TABLE

Parameter	Number of Samples	Sample Matrix	Analytical Method	Holding Time	Container/ Preservative
TCLP Metals	1	Aggregate	1313 1314 1315 1316	6 months	20 2-liter plastic jars

The number of samples does not include QA equipment blanks or duplicate samples.

